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Kohler, B.E.; Song, K.; Buma, W.J.

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Lowest energy excited singlet states of isomers of alkyl substituted hexatrienes

Wybren Jan Buma, Bryan E. Kohler, and Kyuseok Song
Chemistry Department, University of California, Riverside, California 92521

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Vibrationally resolved $S_0 \rightarrow S_1$ excitation spectra for the alkyl substituted linear polyenes heptatriene, octatriene, and decatriene seeded into a supersonic He expansion have been measured by resonance enhanced multiphoton ionization spectroscopy. As is the case for the parent compound hexatriene, the lowest energy excited singlet state in all of these molecules is the 2^1A_g state. The measurement of $S_0 \rightarrow S_1$ excitation spectra of three of the four double bond isomers of heptatriene gives a detailed picture of the dependence of the electronic structure of the 2^1A_g state on molecular conformation. The three isomers for which spectra are presented have the *cis* configuration at either the central or the alkyl substituted double bond, or both. For the case of the mono *cis* species with the *cis* configuration at the alkyl substituted double bond the spectra show the presence of two single bond conformers. Because of the increased number of distinguishable isomers and conformers for octatriene and decatriene we were unable to unambiguously separate the observed spectra of these molecules into contributions from single specific molecular conformations. However, the increased excitation intensity in the low frequency region relative to that in the C–C and C=C stretching region for octatriene and decatriene as compared to heptatriene suggests that vibrational relaxation is enhanced in the more complex molecules. In the case of unsubstituted hexatriene, previously reported spectra show that the 2^1A_g state has lower symmetry than does the ground state (most likely due to nonplanarity at the terminal carbon atoms). There is no evidence for an analogous distortion in the excitation spectra measured for the alkyl substituted hexatrienes.

I. INTRODUCTION

Many biologically important chromophores are conjugated linear polyenes (for example, retinal and β -carotene).^{1–5} Since the original discovery that the 2^1A_g state is the lowest energy excited singlet state in α,ω -diphenyl-1,3,5,7-octatetraene^{6,7} instead of the 1B_u state as predicted by molecular orbital theory at the Hartree–Fock level,^{8,9} a number of studies have elucidated the properties of the 2^1A_g state in linear polyenes with four or more conjugated double bonds in the polyene chain.^{3,10,11} The high resolution studies that have been so effective in characterizing the 2^1A_g state in the longer polyenes have relied on the sensitivity that can be realized by using fluorescence to detect absorption. Because unsubstituted trienes and dienes have immeasurably small quantum yields for fluorescence, different techniques are required to obtain unambiguous spectra of the 2^1A_g state. Recently, we used resonance enhanced multiphoton ionization spectroscopy to measure the $1^1A_g \rightarrow 2^1A_g$ spectrum for *cis*-hexatriene seeded into a supersonic He expansion. The high resolution spectrum showed that, among the other things, the origin of the 2^1A_g state is 5270 cm^{-1} below the origin of the 1B_u state and that, in contrast to what has been found for longer polyenes, the 2^1A_g state distorts to almost isoenergetic nonplanar conformations^{12,13} (although the molecular symmetries of *cis*-hexatriene and most of the alkyl substituted trienes discussed here are lower than C_{2h} , we continue to use the designations A_g and B_u to emphasize the correlation of the observed states to those of the symmetrical unsubstituted all-*trans* polyene).

The photochemistry of vitamin D involves isomerisations of alkyl substituted hexatriene. To understand this photochemistry at a fundamental level we need to develop an understanding of how alkyl substitution affects the hexatriene 2^1A_g state. This was one of the primary motivations for the spectroscopic studies of various alkyl substituted hexatrienes that we report here. By measuring the wavelength dependence of parent ion production by two-photon ionization of molecules seeded into a supersonic jet expansion we have obtained fully resolved $1^1A_g \rightarrow 2^1A_g$ excitation spectra for the isomers and conformers of heptatriene shown in Fig. 1. Our shorthand notation for these species is ZZ heptatriene for Z,Z-1,3,5-heptatriene, ZE heptatriene for Z,E-1,3,5-heptatriene, and EZ heptatriene for E,Z-1,3,5-heptatriene. Spectra were also obtained for octatriene and decatriene, but in these cases we were unable to decompose the measured spectra into contributions from single isomers. In the case of heptatriene where this decomposition was possible, analysis of the measured spectra greatly expands our understanding of the dependence of the properties of the triene 2^1A_g state on alkyl substitution and molecular geometry.

II. EXPERIMENTAL

We have previously published a detailed description of our experimental setup for measuring resonance enhanced multiphoton ionization spectra.¹³ The excitation source is the beam from a Spectra Physics PDL-2 dye laser pumped by a DCR-3 Nd:YAG laser. After frequency doubling by a

FIG. 1. Isomers and conformers of 1,3,5-heptatriene studied in this paper. According to our MM2 calculations the energies relative to the lowest energy conformer of the EE isomer are 1.3 and 3.6 kcal for the two EZ isomers, 1.5 kcal for the ZE isomer and 4.0 kcal for the ZZ isomer.

WEX-1 wavelength extender this excitation beam intersects the molecular beam at the entrance aperture of a time of flight mass spectrometer (R.M. Jordan Co.). The molecular beam is formed by a pulsed valve with a 0.5 mm diameter nozzle (R.M. Jordan Co.) that connects the reservoir containing a mixture of the substituted hexatriene at its equilibrium vapor pressure and 3 atm of He to the vacuum chamber. Ions produced at the intersection of the molecular and laser beams are accelerated through the time of flight mass spectrometer and detected by a dual microchannel plate. The mass peak for the molecular ion was selected and averaged by standard boxcar techniques (the mass resolution of our system at 94 amu is $t/\Delta t = 2000$). The spectrometer is controlled by a HP310 computer which also takes care of data storage and analysis.

Heptatriene, octatriene, and decatene were prepared by the procedure described in Ref. 14. As can be seen in Fig. 2, injection of heptatriene into a capillary gas chromatograph

FIG. 2. Capillary gas chromatogram of 1,3,5-heptatriene. The first band (12.2 minutes) is assigned as the EE isomer, the second band (13.1 minutes) consists of two bands assigned to the EZ and ZE isomer while the last band (14.0 minutes) is assigned to the ZZ isomer. The numbers in the figure correspond to the numbers with which bands are labeled in the excitation spectra of Fig. 3.

graph (Shimadzu GC-14A) with a 25 meter column (liquid phase, 007 series methyl silicon, I.D. 0.32 mm) shows that at least four isomers are present. In the case of hexatriene we found that the *E* isomer has a smaller retention time than does the *Z* isomer. As is discussed further in Sec. III A 1, this is one of the pieces of evidence that with the relative abundances and observed spectra lead to the structural assignments given in Fig. 2.

Samples for the spectroscopic experiments were separated with a preparative gas chromatograph (F&M Laboratory Model 700 Series) using an 8 foot long 1/4 inch diameter column (chromosome P/AW 60/80 mesh support, β,β' -oxydipropionitrile phase). The heptatriene separations were run at a column temperature of 50 °C, an injection temperature of 110 °C, a detector temperature of 180 °C and a He carrier gas flow rate of 50 ml/min. Under these conditions only two distinct peaks could be seen: one for *E,E*-1,3,5-heptatriene or the all-*trans* isomer and one that is the unresolved envelope of peaks for the *ZE*, *EZ*, and *ZZ cis* isomers. To obtain samples with different ratios of the three *cis* isomers we collected the leading or trailing half of the unresolved *cis* peak.

Analysis of octatriene on the capillary gas chromatograph showed that the sample contained at least seven isomers including two isomers of ethyl-hexatriene. With the preparative gas chromatograph using a column temperature of 80 °C, four bands could be distinguished. In order of elution they were: one band for the isomers of ethylhexatriene, one band for the *EEE* isomer of octatriene, and a pair of overlapping bands for octatriene isomers containing a *Z* linkage. In the following we will refer to *EEE* octatriene as *trans*-octatriene and samples collected from the leading and trailing parts of the last band eluted as *cis*(1)-octatriene and *cis*(2)-octatriene, respectively.

Finally, because analysis of our decatene by the capillary gas chromatograph showed at least six closely spaced bands no attempt was made to separate isomers with the preparative instrument.

III. RESULTS AND DISCUSSION

In this section we will first present and discuss the spectra obtained for the isomers for heptatriene where we have succeeded in unambiguously resolving the excitation spectra into the spectra of individual isomers. Then the results obtained for octatriene and decatene where a complete decomposition of the measured spectra into the spectra of individual isomers was not possible will be presented and discussed in the context of the heptatriene results.

A. Excitation spectra of heptatriene

In our previous study of hexatriene we found we could not measure resonance enhanced multiphoton ionization excitation spectra with an acceptably high signal-to-noise ratio for the *trans* isomer.^{12,13} We attributed this to the strict symmetry forbidden character of the $1^1A_g \rightarrow 2^1A_g$ transition for a centrosymmetric *trans* geometry. Thus, it was not a surprise to find that our present apparatus was not sensitive enough to obtain spectra for *EE* heptatriene.

FIG. 3. $1^1A_g \rightarrow 2^1A_g$ excitation spectra of 1,3,5-heptatriene detected using resonance enhanced multiphoton ionization spectroscopy. The upper half of the figure shows the excitation spectrum measured for the leading part of the gas chromatographic peak containing the EZ, ZE, and ZZ isomers, the lower part shows the excitation spectrum measured for the trailing half. The numbers in the spectra refer to bands assigned to the specific isomers: 1 = ZZ, 2 = ZE, and 3 = EZ (see also Tables I, II, and III).

However, reasonable spectra could be obtained for material from the *cis* heptatriene fraction. The upper trace in Fig. 3 shows the spectrum measured for material taken from the leading half of the *cis* isomer fraction, hereafter called sample A. The lower trace in Fig. 3 shows the spectrum measured for the trailing half, hereafter called sample B. The spectra in Fig. 3 have been constructed by linking consecutive scans to each other as described previously.¹³ Since in this case the overlap region used to determine the parameters for linearly scaling one spectrum to the other did not contain any significant bands, the relative intensities of bands from different scans are subject to relatively large errors. Checks of the relative intensities of the major bands show that the errors are no larger than 20%.

From the absorption spectrum of *cis*-heptatriene vapor in equilibrium with the room temperature liquid we estimate that the origin of the $1^1A_g \rightarrow 1^1B_u$ transition is at approximately 256.6 nm. This is shifted by 695 cm^{-1} to lower energy from the location of the $1^1A_g \rightarrow 1^1B_u$ origin determined for jet cooled *cis*-hexatriene.¹⁵ The absorption spectrum of *trans*-heptatriene vapor shows the 0-0 transition at 255.5 nm, which means a shift to lower energy with respect to *trans*-hexatriene by 648 cm^{-1} .¹⁵ Clearly, the spectra in Fig. 3 belong to the $1^1A_g \rightarrow 2^1A_g$ transition.

1. Assignment of excitation spectra to isomers

To assign peaks in the spectra shown in Fig. 3 to particular isomers of heptatriene we must first determine which of the bands in these spectra represent 0-0 transitions. In doing

this it is useful to recall that the most intense fundamental in the $1^1A_g \rightarrow 2^1A_g$ excitation spectrum of any linear polyene is the symmetric C=C stretch vibration. In *cis*-hexatriene this vibration has a frequency of 1724 cm^{-1} in the 2^1A_g state.¹³ Thus, the assignment of a band as a 0-0 transition implies that there must be a relatively intense C=C stretch fundamental roughly 1730 cm^{-1} to higher energy.

In all spectra measured for sample A the lowest energy excitation feature is the band at $33\,809\text{ cm}^{-1}$. Thus, the $33\,809\text{ cm}^{-1}$ band must be the 0-0 transition of one of the heptatriene isomers. This assignment is supported by the presence of a reasonably intense band 1760 cm^{-1} higher in energy which can be assigned as the symmetric C=C stretch fundamental.

Spectra measured for sample B show several bands below $33\,809\text{ cm}^{-1}$: The one at the lowest energy is the very intense band at $33\,475\text{ cm}^{-1}$. The assignment of this band as the 0-0 band for another isomer of heptatriene is supported by the significantly intense band at $33\,475 + 1709\text{ cm}^{-1}$ which we assign as the symmetric C=C stretching mode of this heptatriene isomer.

Samples A and B are prepared by dividing one gas chromatographic band which contains three isomers. Since this separation has been performed many different times, the ratios of the three isomers in the separated samples will inevitably be different in different scans. This means that bands can be divided into groups that have the same relative intensities in all scans. Comparing the upper to the lower trace in Fig. 3 it is apparent that there are a number of bands whose relative intensities are about the same in both spectra. Among these

are the two bands at $34\,237\text{ cm}^{-1}$ and $34\,282\text{ cm}^{-1}$ which correlate with two prominent bands 1720 cm^{-1} to higher energy and two other weak bands 1259 cm^{-1} to higher energy. From this we conclude that the bands at $34\,237\text{ cm}^{-1}$ and $34\,282\text{ cm}^{-1}$ represent the 0–0 transitions of two closely related hexatriene isomers that are distinctly different from the ones responsible for the lowest energy excitation features seen for samples A and B, respectively.

The assignment of a specific heptatriene conformation to each of the four origins uses several lines of argument. First of all, we use the fact that the ZZ isomer has a longer retention time than do the EZ and the ZE isomers. This means that the species whose origin band is $33\,475\text{ cm}^{-1}$ must be the ZZ isomer since it is present only in sample B. Consequently, the origin band at $33\,809\text{ cm}^{-1}$ and the ones at $34\,237\text{ cm}^{-1}$ and $34\,282\text{ cm}^{-1}$ belong to EZ and ZE isomers. Because of the nearly identical vibronic development of the spectra with origins at $34\,237\text{ cm}^{-1}$ and $34\,282\text{ cm}^{-1}$ we believe that they belong to single bond isomers (conformers) of a single double bond isomer, either EZ or ZE. In principle, the doubled spectra could represent different conformations in the ground state, the $2\,^1A_g$ state, or both (previous studies have shown that conformers present in the ground state can be frozen out in a supersonic jet expansion at the ratio that reflects equilibrium at the reservoir temperature.^{16,17}). Since this doubling is not observed for any of the other isomers, we believe that it reflects the presence of two different ground state conformers with distinct, albeit very similar, $2\,^1A_g$ states. Using only the measured spectra and gas chromatographic behaviors, we are not able to arrive at a unique assignment of the four origins to molecular conformations. Thus, we have augmented the available information with quantum chemical calculations of relative stabilities.

To decide whether the origin at $33\,809\text{ cm}^{-1}$ belongs to the ZE isomer and the origins at $34\,237\text{ cm}^{-1}$ and $34\,282\text{ cm}^{-1}$ belong to conformations of the EZ isomer or vice versa, we have performed MM-2 calculations of ground state energy as a function of conformation.^{18,19} Though we are well aware that there may be substantial errors in the calculated values of the absolute energies, the highly empirical nature of the MM-2 method should give a reasonably accurate picture of the relative energies.

TABLE I. Vibrational assignments of tCtC-heptatriene. The numbers in brackets give the deviation from the harmonic approximation.

Frequency (cm^{-1})	$\Delta\nu(\text{cm}^{-1})$	Assignment
33 475	0	(0–0)
33 540	65	ν_1
33 608	133	$2\times\nu_1$
33 621	146	ν_2
33 629	154	ν_3
33 692	217	ν_4
35 184	1709	ν_5 (C=C)
35 339	1864	$\nu_2 + \nu_5$ (+ 1)
35 401	1926	$\nu_4 + \nu_5$ (0)
35 471	1996	ν_6

TABLE II. Vibrational assignments of tCtT-heptatriene. The numbers in brackets give the deviation from the harmonic approximation.

Frequency (cm^{-1})	$\Delta\nu(\text{cm}^{-1})$	Assignment
33 809	0	(0–0)
33 926	117	ν_1
33 964	155	ν_2
33 996	187	ν_3
34 022	213	ν_4
34 041	232	$2\times\nu_1$ (– 2)
34 118	309	$2\times\nu_2$ (– 1)
34 162	353	$3\times\nu_1$ (– 2)
34 413	604	ν_5
35 569	1760	ν_6 (C=C)

Only in the case of the EZ isomer do we find two single bond isomers with a sufficiently small ground state energy difference (2.3 kcal/mole) that it is plausible that both could be present under room temperature equilibrium conditions. The single bond isomers of the ZE isomer are much further apart in energy (3.5 kcal/mole). Thus, the MM-2 calculations support the assignment of the origins at $34\,237\text{ cm}^{-1}$ and $34\,282\text{ cm}^{-1}$ to two single bond isomers of the EZ isomer and the origin at $33\,809\text{ cm}^{-1}$ to the *s-trans* conformer of the ZE isomer.

In summary, the assignment of molecular structures to spectra that is consistent with all available data is the following: the origin located at $34\,475\text{ cm}^{-1}$ belongs to the lowest energy conformer of the ZZ isomer (tCtC-heptatriene), the origin at $33\,809\text{ cm}^{-1}$ to the lowest energy conformation of the ZE isomer (tCtT-heptatriene), and the origins at $34\,237\text{ cm}^{-1}$ and $34\,282\text{ cm}^{-1}$ to two conformers of the EZ isomer (tTtC- and cTtC-heptatriene).

2. Vibrational analysis

The vibrational assignments of the excitation spectra of ZZ, ZE, and EZ heptatriene are summarized in Tables I, II, and III, respectively. As is the general situation for polyenes the symmetric C=C stretching mode is strongly active in these spectra and has a significantly higher frequency in the $2\,^1A_g$ excited state than in the ground state. IR spectra show that the C=C stretch vibration in the ground state has a frequency of 1627 cm^{-1} for sample A and 1624 cm^{-1} for

TABLE III. Vibrational assignments of tTtC and cTtC-heptatriene.

Frequency (cm^{-1})	$\Delta\nu(\text{cm}^{-1})$	Assignment
34 237	0	A(0–0)
34 263	26	A(0–0) + ν_1
34 282	45	B(0–0)
34 307	25	B(0–0) + ν_1
34 325	42	B(0–0) + ν_2
34 337	56	B(0–0) + ν_3
34 348	67	B(0–0) + ν_4
35 496	1259	A(0–0) + ν_5 (C–C)
35 550	1258	B(0–0) + ν_5 (C–C)
35 956	1719	A(0–0) + ν_6 (C=C)
36 002	1720	B(0–0) + ν_6 (C=C)

sample B.²⁰ This increase in frequency upon excitation reflects the intrinsic electronic character of the 2^1A_g state²¹ which may be explained in terms of vibronic mixing of the 1^1A_g and 2^1A_g states.²²

The frequency of the C=C stretching mode in the 2^1A_g state is significantly different for the three heptatriene double bond isomers. In unsubstituted *cis*-hexatriene it is 1724 cm^{-1} .¹³ Adding a methyl group *trans* to the terminal double bond induces a shift to higher frequency (1760 cm^{-1} for ZE heptatriene) while adding a methyl group *cis* to the terminal double bond induces a shift to lower frequency (1709 cm^{-1} for ZZ heptatriene). This sensitivity to double bond conformation stands in contrast to the insensitivity of the frequency of this mode to single bond conformation (1720 cm^{-1} for both single bond isomers of EZ heptatriene). While the basis for the strong dependence on conformation about the terminal double bond is not clear, the increase in C=C stretch frequency in the 2^1A_g state with increasing number of *trans* double bond linkages is consistent with what has previously been observed for octatetraene.^{23–25}

Whereas the intensity of the C=C stretching mode is relatively strong in the excitation spectra of all three double bond isomers, the C–C stretching mode is only observed as a very weak feature for the EZ isomer. Since experiments on octatetraene have demonstrated that the intensity of the C–C stretching mode is strongly influenced by small perturbations,²⁶ this could explain the absence of this mode in the excitation spectra of the other two isomers.

In addition to the C=C and C–C stretching modes, a number of low frequency vibrations are active in the spectra as seen in Fig. 3 and Tables I–III. Similar activity in low frequency modes was seen for *cis*-hexatriene as well although in that case the intensity was significantly lower than the intensity of the symmetric C=C stretching mode. This is not the case for the isomers of heptatriene where some of the low frequency modes have greater relative intensity than does the C=C stretch vibration. This indicates that the torsional and bending vibrations are even more involved in the changes of equilibrium geometry upon excitation to the 2^1A_g state in heptatriene than they are in *cis*-hexatriene. Among the significantly active low frequency modes are the ones at 154 cm^{-1} and 217 cm^{-1} in the ZZ isomer and the ones at 155 cm^{-1} and 213 cm^{-1} in the ZE isomer whose frequencies are nearly identical to the 155 cm^{-1} and 250 cm^{-1} modes seen in the excitation spectrum of *cis*-hexatriene.^{12,13}

The mode at 117 cm^{-1} that forms the most intense progression in the spectrum of the ZE isomer has no counterpart in the spectrum of *cis*-hexatriene. This suggests that this mode involves the hindered rotation of the CH_3 group and that in the ZE isomer there are appreciable changes in the orientation of the CH_3 group upon excitation to the 2^1A_g state.

We are left with a puzzle which is the assignment of the band 1996 cm^{-1} above the origin of the ZZ isomer. This frequency is too high to be assigned as another C=C stretching mode: There is no precedent for a fundamental with this high of a frequency in the 2^1A_g state of a short linear polyene.²⁷ A possible assignment of this band could be that it is

the 0–0 transition of another conformer. The relatively small differences in 0–0 transition energies measured for other isomers makes this assignment unlikely. Further, in a careful search 1600 cm^{-1} to 1800 cm^{-1} higher in energy we were unable to locate any feature that could be attributed to a C=C stretch fundamental added to this band. This leaves the assignment of 1996 cm^{-1} band in the spectrum of ZZ heptatriene as the overtone of a nontotally symmetric $\approx 1000\text{ cm}^{-1}$ fundamental. Such an assignment is buttressed by the fact that there are several nontotally symmetric modes around 1000 cm^{-1} in the ground states of EE and EZ (or ZE) heptatriene.^{20,28} In the case of EE octatetraene a comparison of one-photon and two-photon fluorescence excitation spectra has shown some vibronic bands were in fact overtones in nontotally symmetric modes.²³

3. Properties of the 2^1A_g state

A comparison of the results obtained for heptatriene to those previously reported for hexatriene shows that while substituent induced shifts in electronic excitation energies are relatively small, there are significant differences in the vibronic development of the $1^1A_g \rightarrow 2^1A_g$ excitation spectrum. In hexatriene, as in other unsubstituted polyenes, most of the vibronic intensity is concentrated in the fundamental and overtones of the symmetric C=C stretch vibration. This is not the case for the isomers and conformers of heptatriene: the C=C stretch fundamental has an intensity that is only roughly equal to those of the low frequency vibrations in the EZ isomer and that is smaller than the intensities of those vibrations in the ZE and ZZ isomers.

In the 2^1A_g state the equilibrium geometry of hexatriene (unsubstituted heptatriene) distorts to two nonplanar geometries.^{12,13} This distortion produces a 5 cm^{-1} splitting of the $1^1A_g \rightarrow 2^1A_g$ origin band and multiplet structures for the low frequency vibrations. Further, combinations and overtones of the low frequency vibrations exhibit significant anharmonicity as would be expected for a double minimum potential. There is no evidence for a similar distortion in the 2^1A_g states of any of the isomers and conformers of heptatriene. The 0–0 transitions and all vibronic features appear as a single line with widths limited by the bandwidth of the laser. This and the fact that the low frequency vibronic features exhibit less anharmonicity suggests that the ground and excited state potential surfaces both have single minima.

One might expect that the vibronic development of the $1^1A_g \rightarrow 2^1A_g$ excitation spectra of the various isomers of heptatriene would be very similar. This is not the case. The degree to which the low frequency fundamentals are important in the vibronic development depends strongly on the ground state conformation. In the excitation spectrum of the ZZ isomer the 0–0 transition is the most intense band in the spectrum and the band at 154 cm^{-1} is the most intense fundamental. In the case of the ZE isomer the 0–0 band is less intense than the 117 cm^{-1} fundamental that dominates the vibronic development of the spectrum. In the EZ isomer the 0–0 band and the C=C stretch fundamental have roughly equal intensities and the low frequency vibrations make almost no contribution to the vibronic development. This

FIG. 4. $1^1A_g \rightarrow 2^1A_g$ excitation spectra of octatriene. The main body of the figure shows the spectrum obtained for the leading part of the gas chromatographic peak containing the isomers with at least one *Z* linkage. The insert in the figure includes the peaks which can only be detected for the trailing part of this peak.

means that the details of changes in equilibrium geometries are quite different for the different isomers.

B. Octatriene and decatene

The resonance enhanced two-photon ionization spectrum of the *cis*(1) fraction of octatriene is shown in Fig. 4. As was the case for the *cis* fraction of heptatriene, this spectrum is the sum of spectra of several isomers and conformers of octatriene. The inset in Fig. 4 shows a set of weak narrow bands that are only observed for the *cis*(2) fraction octatriene. By analogy to heptatriene we tentatively assign the lowest energy band in the insert ($33\,309\text{ cm}^{-1}$) as the origin of the $1^1A_g \rightarrow 2^1A_g$ transition of an isomer of octatriene that contains at least one *Z* linkage and the band at $33\,562\text{ cm}^{-1}$ (the lowest energy band seen in the main spectrum in Fig. 4) as the 0-0 transition of another octatriene isomer that contains at least one *Z* linkage.

Even though the octatriene excitation spectra cannot be decomposed into the spectra of individual isomers, Fig. 4 clearly shows that for all the isomers vibronic intensity is concentrated in the low frequency region: Fundamentals of the symmetric C=C and C-C stretch vibrations are not seen. The density of band in the low frequency region of the spectrum is much higher than was the case for either hexatriene or heptatriene. Because of the increased molecular complexity and sample heterogeneity a detailed vibrational analysis at this time is impossible. However, we note that above $34\,200\text{ cm}^{-1}$ (approximately 650 cm^{-1} above the onset of excitation intensity) the sharp vibronic bands disappear into a very broad feature. We can suggest three possible explanations. First, and we think most likely, this could re-

fect band broadening due to increased rates of internal energy redistribution since methyl substitution is known to enhance internal vibrational relaxation.²⁹ Second, it may be due to vibronic structure that is simply too dense to be resolved with our current setup. Third, it could be that multiphoton ionization events other than the $1 + 1$ process are enhanced in this region.

The excitation spectrum for $1^1A_g \rightarrow 2^1A_g$ resonance enhanced two-photon ionization of decatene is shown in Fig. 5. Since no attempts were made to separate this sample into individual isomers, this is certainly the superposition of a number of different spectra. It seems reasonable that the most intense band in the spectrum (the one located at $33\,868\text{ cm}^{-1}$) is the 0-0 transition of a decatene isomer with at least one *Z* linkage. Beyond this little can be said except to remark that the symmetric C=C and C-C stretch fundamentals are not seen and that the vibronic development is even more intense and complex in the low frequency region than was the case for octatriene. The excitation spectrum of decatene has a broad feature analogous to that observed for octatriene although the energy separation of this broad feature from the onset of the excitation spectrum is somewhat smaller (about 350 cm^{-1} for decatene versus about 650 cm^{-1} for octatriene).

The importance of low frequency modes in the vibronic development of the $1^1A_g \rightarrow 2^1A_g$ excitation spectrum increases with the addition of methyl groups to the hexatriene skeleton. In the case of unsubstituted hexatriene the vibronic development closely resembles that observed for other unsubstituted polyenes: the symmetric C=C stretch vibration dominates the spectrum. In heptatriene progressions in the

FIG. 5. $1^1A_g \rightarrow 2^1A_g$ excitation spectrum of decatatriene. Since no attempt was made to separate the sample into isomers this spectrum represents the superposition of the spectra of all isomers present in the sample.

low frequency modes are at least as active as the symmetric $C=C$ stretching mode. Finally, in octatriene and decatatriene the symmetric $C=C$ stretching mode is not seen and the vibronic development is restricted to the low frequency region. This is consistent with the idea that alkyl substitution significantly increases the rate of vibrational energy redistribution in the 2^1A_g state of hexatriene.

C. All-*trans*-trienes

Because the $1^1A_g \rightarrow 2^1A_g$ transition in *trans*-hexatriene is both configurationally and symmetry 1-photon forbidden, we have not yet been able to observe a well developed $1 + 1$ resonance enhanced two-photon ionization excitation spectrum for this isomer. This is also true for EE heptatriene, which implies that the substitution of a single methyl group to the terminus of the hexatriene skeleton does not significantly break the symmetry of the 2^1A_g state.

The situation is different for EEE octatriene. Figure 6 shows that for this molecule the cross section for one-photon excitation of the 2^1A_g state is large enough that we can, for the first time, observe the 2^1A_g state of an all-*trans* triene in the gas phase. The lowest energy band in the $1^1A_g \rightarrow 2^1A_g$ excitation spectrum is at $34\,291\text{ cm}^{-1}$. As was the case in the excitation spectra of the other isomers of octatriene, the vibronic development is restricted to the low frequency region: the fundamental of the symmetric $C=C$ stretching mode is not observed.

The observation of a one-photon $1^1A_g \rightarrow 2^1A_g$ excitation spectrum for EEE octatriene and the absence of such spectra for the all-*trans* isomers of hexatriene and heptatriene is puzzling. In first instance one would try to explain

the spectrum of Fig. 6 as originating from a conformer which is *s-cis* to at least one of the single bonds. MM2 calculations rule out such an explanation since they indicate that the energy difference between *s-trans* and *s-cis* conformers is about the same in hexatriene, heptatriene and octatriene. Though our experiments show that the electronic symmetry of the hexatriene skeleton is increasingly affected by an increasing number of methyl substituents they do not as yet allow for a detailed explanation of this symmetry breaking. It is however interesting to note that recent experiments on methyl substituted octatetraenes have shown results which seem to indicate an analogous increase of transition dipole moment upon methyl substitution as that observed here for substituted hexatrienes.³⁰

IV. CONCLUSIONS

We have obtained resonance enhanced two-photon ionization excitation spectra for the lowest energy excited singlet states of heptatriene, octatriene and decatatriene. In all cases this state is the 2^1A_g state as is true for hexatriene. In the case of heptatriene we have been able to decompose the observed spectra into the spectra of four different isomers whose structures are assigned on the basis of abundance, gas chromatographic behavior and energy as estimated by MM-2 calculations. This allows a detailed determination of the changes in the electronic character of the 2^1A_g state that follow from methyl substitution at the terminal carbon. Unlike *cis*-hexatriene where the vibronic development in the 2^1A_g state is dominated by the symmetric $C=C$ stretch vibration, the low frequency modes are very important in the

FIG. 6. $1^1A_g \rightarrow 2^1A_g$ excitation spectrum of EEE octatriene.

vibrational structure of the $1^1A_g \rightarrow 2^1A_g$ transition in heptatriene. Further, in heptatriene the intensity distribution in the vibrational fine structure strongly depends on the molecular geometry. In octatriene and decatatriene the vibrational development in the $1^1A_g \rightarrow 2^1A_g$ excitation spectrum is completely limited to the low frequency region, which points to an increase in the importance of vibrational relaxation effects with increasing alkyl substitution of the hexatriene skeleton. None of the alkyl substituted hexatrienes exhibited the multiplet structures seen for *cis*-hexatriene and attributed to an out of plane distortion in the 2^1A_g state. If our assignment of chromatographic peaks for octatriene is correct, dimethyl substitution can induce enough one-photon absorption cross section as to allow us, for the first time, to observe the 2^1A_g state for an all-*E* polyene in the gas phase.

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