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Lowest energy excited singlet state of isolated *cis*-hexatriene

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In a previous letter [J. Chem. Phys. **92**, 4622 (1990)] we reported the first observation of the 2^1A_g state of *cis*-hexatriene in a supersonic jet expansion by using resonance enhanced multiphoton ionization spectroscopy. Here, the vibrational analysis of the $1^1A_g \rightarrow 2^1A_g$ excitation spectrum of *cis*-hexatriene is presented. The excitation spectrum shows that *cis*-hexatriene in the 2^1A_g state deviates slightly from planarity; a conclusion which is corroborated by *ab initio* calculations indicating that the nonplanarity primarily involves the terminal hydrogen atoms. Except for observable intensity in the low frequency modes associated with the small out of plane distortion, the vibronic development of the $1^1A_g \rightarrow 2^1A_g$ transition in *cis*-hexatriene is similar to that observed for other polyenes: the 0-0 transition is the most intense feature and the next most intense band is the C=C stretching fundamental. Thus the general features of the electronic structure of the *cis*-hexatriene 2^1A_g state are analogous to those of other polyenes.

I. INTRODUCTION

Linear polyenes have long attracted considerable interest, in part because they constitute a class of molecules of fundamental importance in biological systems. Consequently, many experimental as well as theoretical studies have been devoted to the elucidation of the electronic structure of these molecules in order to come to an understanding of their photophysical and photochemical properties.¹ One of the more intriguing aspects of this electronic structure is found in the ordering of the excited singlet states.²⁻⁴ Molecular orbital theory at Hartree-Fock level predicts that the lowest excited singlet state is the configuration where one electron is excited from the highest energy molecular orbital occupied in the ground state to the lowest energy unoccupied molecular orbital, which in the all-*trans* polyenes results in a state of B_u symmetry. In contrast to this prediction, experimental studies have found that for linear polyenes with four or more double bonds the lowest excited singlet state is the 2^1A_g state^{2,3}; a state which can loosely be characterized as a two-electron excitation.

While subsequent studies have established a detailed understanding of the 2^1A_g state of linear unsubstituted polyenes with four or more double bonds,⁵⁻⁹ this is not true for the shorter polyenes hexatriene and butadiene for which even the ordering of the excited singlet states has remained a subject of controversy.¹⁰⁻¹⁵ Furthermore, until this work, information on the 2^1A_g state has been derived from the study of unsubstituted polyenes in the solid phase or substituted polyenes in the solid and gas phase. This is the first case in which it has been possible to obtain vibrationally resolved spectra of the 2^1A_g state of an unsubstituted polyene in the gas phase.

In this report we give a detailed analysis of the $1^1A_g \rightarrow 2^1A_g$ excitation spectrum of *cis*-hexatriene. Not only is this molecule important from a biological point of view since it is the chromophore for vitamin D photochemistry, but a knowledge of its electronic properties will also contribute to a better understanding of the dependence of the electronic structure of polyenes on the number of double bonds.

The study of the excited states of hexatriene has been greatly hampered by the absence of fluorescence in this molecule. Though the 1^1B_u state is by now well characterized by application of direct absorption spectroscopy,¹⁶ it is clear that such an approach is not possible for the, in first approximation forbidden, 2^1A_g state. For the study of this state one has to use techniques which do not depend on the molecule having a significant emission yield. With this in mind it appeared to us that resonance enhanced multiphoton ionization (REMPI) spectroscopy¹⁷ would offer a promising strategy for studying the 2^1A_g state in hexatriene.

In a recent communication we reported the first successful results of such a study.¹⁸ By measuring REMPI excitation spectra for *cis*-hexatriene in a supersonic jet expansion we were able to directly observe the 2^1A_g state of *cis*-hexatriene (although in C_{2v} *cis*-hexatriene the symmetry labels are A_1 and B_2 instead of A_g and B_u , respectively, to emphasize the connection to the states of the *trans*-isomers we will continue to use the C_{2h} labels). These results showed, in contrast to previous calculational results¹² and results inferred from experimental studies,^{13,15} that the 2^1A_g state in hexatriene is indeed below the 1^1B_u state.

This paper presents a complete vibrational analysis of the *cis*-hexatriene $1^1A_g \rightarrow 2^1A_g$ REMPI excitation spectrum. This analysis shows that the main electronic characteristics of the 2^1A_g state of *cis*-hexatriene agree well with those previously derived for longer polyenes. However, with respect to the detailed geometry of the 2^1A_g state there are important differences. In the studies performed up till now on longer polyenes it was concluded that the molecules remain planar upon excitation. The excitation spectrum of *cis*-hexatriene reveals that this is not the case for this molecule. We also present preliminary results of *ab initio* calculations that indicate that this deviation from planarity is mainly localized on the terminal hydrogen atoms.

II. EXPERIMENTAL

Hexatriene was purchased from Aldrich Chemical Co. as an equilibrium mixture of *cis*- and *trans*-isomers. *Cis*-hex-

atriene was separated from this material by gas chromatography using a column packed with 10% β,β' -oxidipropionitrile on 60/80 mesh Chromosorb P/AW. In our experiments a molecular beam, made by a free jet expansion of *cis*-hexatriene vapor mixed with 3 atm He, was intersected at right angles by the focused beam of the excitation laser. Ions generated at the intersection point were accelerated along the third orthogonal direction into a time of flight (TOF) mass spectrometer. A schematic diagram of the experimental setup for this type of REMPI spectroscopy is shown in Fig. 1.

The excitation source was the frequency doubled output of a dye laser (Spectra Physics PDL-2) pumped by a Nd:YAG laser (Spectra Physics DCR-3). The dyes used in the present study were rhodamine 640, rhodamine 610, rhodamine 590, fluorescein 548, and coumarin 500. In addition, several mixtures of the rhodamine dyes were used in order to obtain a more or less constant dye laser output over the entire energy region. Coumarin 500 was pumped by the third harmonic of the Nd:YAG laser (355 nm), the other dyes were pumped by the second harmonic (532 nm). Frequency doubling of the fundamental was performed by a Spectra Physics WEX-1 wavelength extender. The frequency doubled light (≈ 8 ns temporal width, ≈ 1 cm $^{-1}$ energy width) was focused into the excitation region by a 20 cm focal length lens. The wavelength readout of the dye laser was calibrated by scanning it with a 1.5 m Jobin-Yvon monochromator with a 110 $\times$ 110 mm 2400 line/mm holographically ruled grating. In turn, the wavelength readout of the monochromator was calibrated by scanning over lines from a low-pressure Hg lamp.

The pulsed supersonic expansion was gated by a valve (R. M. Jordan Co.) with a nozzle diameter of 0.5 mm. This valve generates molecular beam pulses of 55 μ s duration. The pulsed valve was triggered by the Nd:YAG laser which operated at 10 Hz. Expansion occurred into a differentially pumped vacuum system consisting of two chambers separated by a beam skimmer with a diameter of 1 mm (Beam Dynamics). A TOF mass spectrometer (R. M. Jordan Co.) is incorporated in the inner chamber. This mass spectrometer is 140 cm long and is equipped with a three stage amplification microchannel plate (Galileo Electrooptic Corp.).

The main chamber was pumped by an Edwards High Vacuum EH2600 Roots blower backed by an Edwards E2M275 mechanical pump to give a pumping rate of 528 l/s. The mass spectrometer chamber was pumped by an Edwards ETP 10/1000 turbomolecular pump (1400 l/s) backed by an Edwards E2M18 mechanical pump (5.5 l/s), both pumps being controlled by an Edwards ETC 1000 turbocontroller. Under the common experimental conditions of 3 atm He backing pressure, this system had a pressure of 2×10^{-7} Torr in the mass chamber and 10^{-5} Torr in the main chamber. In terms of the vibrational temperature of the molecules in the supersonic beam, this setup is capable of cooling down to about 30 K as assessed from measurements of the relative intensities of the 0-0 band and a hot band of aniline.

The ion signal detected by the microchannel plate is amplified by a fast preamplifier (Stanford Research SR240) whose output is connected to both a boxcar integrator (Stanford Research SR250) and a digital oscilloscope (Hewlett

FIG. 1. Schematic overview of the experimental setup (see the text for details).

Packard 54502A). On the oscilloscope the mass spectrum is captured and can be read in by a Hewlett Packard 310 computer. The boxcar is used for mass selective monitoring of a specific ion signal. The output from the boxcar is connected to a multimeter (Hewlett Packard 78A) which is also read out by the computer. In our experiments the overall mass resolution of the TOF system was 1700 at the molecular mass of hexatriene.

For the normalization of the ion signal a reflection of the excitation light was detected by a Laser Precision Rj7200 energy meter with an RTP735 detector head. The readout of this energy meter was also interfaced to the HP310 computer.

In a typical experiment the dye laser was scanned by the computer in steps of $0.1 \text{ \AA}$, although in congested regions of the spectrum steps of $0.05 \text{ \AA}$ have also been used. The ion signal at $m/e = 80$ (the mass of hexatriene) was integrated for 8 s during which time the laser energy was averaged as well. For regions of the spectrum where the resulting signal to noise ratio was not satisfactory, the same procedure was performed for 16 s. Kinetic analyses of experiments in which both the laser pulse energy and the ion signal were read on every laser shot established that this averaging did not significantly distort the measured cross sections.

III. RESULTS AND DISCUSSION

A. The excitation spectrum

In Fig. 2 the excitation spectrum for the $1^1A_g \rightarrow 2^1A_g$ transition of *cis*-hexatriene is shown. This spectrum has been constructed by linking consecutive scans by linearly scaling one scan to the other. The appropriate scaling parameters have been determined by least squares fitting one of the spec-

tra to the other in the region where they overlapped. Care has been taken to see that this region always included at least one excitation feature. Because of error propagation such a procedure has the inherent danger of giving an inaccurate picture of the relative intensities, especially in our case since in most regions the bands in the overlap region had only a poor signal to noise ratio. As a further check, we have therefore performed separate measurements of the intensity of the most prominent bands in the spectrum and compared these intensities with intensities in Fig. 2. From these measurements we can conclude that the relative intensities in Fig. 2 are accurate within 10%.

B. Nature of the resonance

That the spectrum in Fig. 2 derives from a resonance enhancement due to the 2^1A_g state is made clear by the dependence of the magnitude of the ion signal at the origin on the laser pulse energy shown in Fig. 3. This power dependence has been fit by the kinetic expressions for several ionization models. In these fits the laser beam at the focal point has been assumed to be a uniformly illuminated spot with a diameter of 0.1 mm . Under the assumption that the excitation pulse can be represented as a sequence of constant intensity intervals whose midpoints coincided with a smooth Gaussian curve (50 steps for a 8 ns FWHM Gaussian pulse), the number of ions produced by a laser pulse with a given integrated intensity can then be rapidly and accurately calculated. It should be realized that this representation of the laser beam is a highly idealized description since the actual laser beam has a "donut" spatial profile. Consequently, cross sections derived from the fits are an upper limit of the actual cross sections. While the fact that the spatial profile was not accurately modeled means that absolute cross sections are

FIG. 2. $1^1A_g \rightarrow 2^1A_g$ excitation spectrum of *cis*-hexatriene as detected by resonance enhanced two photon ionization spectroscopy. The lower energy scale gives the absolute energy in cm^{-1} , the upper energy scale gives the energy with respect to the 0-0 transition located at $34\,393 \text{ cm}^{-1}$.

FIG. 3. Dependence of the ion signal at $m/e = 80$ on the laser power. The excitation energy is $34\,388\text{ cm}^{-1}$. The solid line represents the best fit to the $1 + 1$ ionization model, the broken line the best fit to a two-photon direct ionization model.

approximate at best, we believe that errors in the relative values are less than 10%.

As seen in Fig. 3 a fit using the $1 + 1$ ionization model, i.e., one photon to the resonant state followed by one photon to the ionization continuum, yields a far better agreement with the experimental data than does a fit using a direct two-photon ionization model. In principle, signals like those in Fig. 2 could arise from two-photon excitation to a Rydberg state. Previous studies of the Rydberg states in hexatriene show that no Rydberg state is present in the energy region at twice the energy of Fig. 2.¹⁹ Analogous fits by other models as, for example, the $2 + 1$ model, show that indeed the state responsible for the resonance enhancement is reached by a one-photon absorption and not by a higher order process. Thus it follows that we are dealing here with the $2\ ^1A_g$ state.

The fit of the power dependence of the ion signal by the $1 + 1$ ionization model gives two solutions with an equal standard deviation. In the first solution the cross section for the first step is small, $(6.9 \pm 0.2) \times 10^{-20}\text{ cm}^2\text{ photon}^{-1}\text{ molecule}^{-1}$, and the cross section for the second step is much larger, $(4 \pm 2) \times 10^{-18}\text{ cm}^2\text{ photon}^{-1}\text{ molecule}^{-1}$. In the second solution the excitation cross section is $(2 \pm 1) \times 10^{-18}\text{ cm}^2\text{ photon}^{-1}\text{ molecule}^{-1}$ and the ionization cross section is $(1.4 \pm 0.5) \times 10^{-19}\text{ cm}^2\text{ photon}^{-1}\text{ molecule}^{-1}$. Since the fits by the various ionization models have shown that the resonance enhancement is a one-photon resonance with the electronically forbidden $2\ ^1A_g$ state, it is the first solution that is the correct one. If the second solution were correct the calculated cross section shows that this state would have been observed in the absorption experiments of Leopold *et al.*¹⁶

C. General features

The origin of the $2\ ^1A_g$ state is a doubled band with maxima at $34\,388$ and $34\,393\text{ cm}^{-1}$ (see also Fig. 4). The observation of the origin at this low energy clearly resolves earlier disputes concerning the ordering of the $2\ ^1A_g$ and 1B_u states in hexatriene since previous direct absorption studies on the free molecule have shown that the origin of the 1B_u state in *cis*-hexatriene is located at $39\,666\text{ cm}^{-1}$,¹⁶ about 5270 cm^{-1} above the origin that has been located here. The presence of the 1B_u state above the $2\ ^1A_g$ state explains why the signal in Fig. 2 gets larger as the excitation energy increases, since it is to be expected that vibronic coupling will make an increasing contribution to the absorption strength as the energy gap between the coupled levels decreases.

FIG. 4. Low energy region of the $1\ ^1A_g \rightarrow 2\ ^1A_g$ excitation spectrum of *cis*-hexatriene. The inserts show the multiplet structure in some of the vibrational bands. These inserts are expanded by a factor of 2 in energy and by a factor of 7 in intensity.

As seen in Fig. 2, the 0–0 transition is one of the more intense bands in the spectrum. From this we infer that the vertical excitation energy of the 2^1A_g state will not be appreciably different from the 0–0 transition energy. We estimate on the basis of the ratio of the intensity of the symmetric C=C stretch vibration and the intensity of the 0–0 transition that the difference between the vertical excitation energy and the 0–0 transition energy is about 2500 cm^{-1} .⁹ Since this energy difference is derived under the assumptions that the vibrational coordinates can be treated as independent harmonic modes and that vibronic coupling is negligible it is clear that this number can only be regarded as an upper limit for the actual energy difference.

Another conclusion drawn from the observation that the 0–0 transition carries such a large intensity concerns the importance of the symmetry properties, most notably the absence of inversion symmetry in *cis*-hexatriene. In the all-*trans* polyenes the $1^1A_g \rightarrow 2^1A_g$ transition is not only forbidden on electronic grounds (to the extent that the 2^1A_g state is represented by a double excitation from the ground state configuration), but also on symmetry grounds. Consequently, when C_{2h} symmetry is realized the 0–0 transition cannot be detected in one-photon excitation and the one-photon ex-

citation spectrum is built on false origins of b_u symmetry vibrations from which vibronic intensity is derived.⁵ In *cis*-hexatriene this is clearly not the case. Though the transition to the 2^1A_g state is still to some extent forbidden on electronic grounds (see also the measured cross section), the absence of inversion symmetry makes the transition symmetry allowed. The absence of any prominent false origin indicates that the transition moment resulting from the symmetry relaxation must be significantly larger than the transition moment derived from vibronic coupling with the 1^1B_u state. The fact that the one-photon excitation profile for the $1^1A_g \rightarrow 2^1A_g$ transition assumes the vibronic development of a symmetry allowed transition under very subtle distortions from C_{2h} symmetry has been thoroughly demonstrated in the case of *trans*-octatetraene in low temperature *n*-alkane crystals.²⁰

D. Overall vibronic development

In Table I we present the results of the vibrational analysis of the spectrum shown in Fig. 2. The 33 most distinct bands present in Fig. 2 can be assigned as overtones or combinations of nine fundamental frequencies.

TABLE I. Vibrational analysis of the $1^1A_g \rightarrow 2^1A_g$ excitation spectrum of *cis*-hexatriene.

Frequency ^a (cm^{-1})	Assignment	Deviation from harmonic approximation (cm^{-1})	Integrated intensity
–5	0–0 (<i>A</i>)		0.9
0	0–0 (<i>B</i>)		1.7
67	ν_1		0.2
152	ν_2		0.2
249	ν_{3a}		0.1
260	ν_{3b}		0.1
360	ν_4		0.2
440	ν_5		0.05
629	ν_6		0.1
892	ν_7		0.03
1123	ν_8 (C–C stretch)		0.3
1318	$\nu_7 + \nu_5$	–14	0.1
1376	$\nu_8 + \nu_{3a,b}$	+1	0.1
1475	$\nu_8 + \nu_4$	–8	0.3
1722;1726	ν_9 (C=C stretch)		2.9
1807	$\nu_9 + \nu_1$	+18	0.4
1886	$\nu_9 + \nu_2$	+12	0.5
2000	$\nu_9 + \nu_{3a,b}$	+12	1.0
2091	$\nu_9 + \nu_4$	+9	1.8
2244	$2 \times \nu_8$	+2	0.1
2362	$\nu_9 + \nu_6$	+11	0.4
2614	$\nu_9 + \nu_7$	0	0.7
2706	...		0.4
2766	...		0.2
2842	$\nu_9 + \nu_8$	–5	2.3
3080;3119	$\nu_9 + \nu_8 + \nu_{3a,b}$	+3	1.3
3204	$\nu_9 + \nu_8 + \nu_4$	+2	1.0
3433	$2 \times \nu_9$	–13	3.0
3793	$2 \times \nu_9 + \nu_4$	0	0.9
3958	$2 \times \nu_8 + \nu_9$	–12	1.5
4137	...		0.2

^aFrequency in cm^{-1} with respect to origin of transition *B* located at $34\,393\text{ cm}^{-1}$.

As is the general situation for polyenes studied so far, the most intense bands in the excitation spectrum are associated with the symmetric C=C stretch vibration and its overtones and combinations with other vibrations. The frequency of this vibration in the 2^1A_g state is 1724 cm^{-1} , which is 102 cm^{-1} higher than the frequency of the corresponding vibration in the ground state.²¹ This frequency increase is a phenomenon generally observed in the 2^1A_g state and is the result of the electronic character of this state as has been discussed recently.²² A similar, though smaller, increase is observed for the symmetric C-C stretch vibration: in the 2^1A_g state a frequency of 1123 cm^{-1} is measured compared with the ground state frequency of 1084 cm^{-1} .²¹

We next turn our attention to the low-frequency energy region of the $1^1A_g \rightarrow 2^1A_g$ excitation spectrum. The main bands in this region are at 67, 152, 249, 260, and 360 cm^{-1} with smaller bands at 440, 629, and 893 cm^{-1} . In comparison with, e.g., octatetraene, this signifies a dramatic increase in the activity of the torsional and bending vibrations. This is partially to be expected on the basis of the change in symmetry but even in *cis-trans*-1,3,5,7-octatetraene only four bands with reasonable intensity in the $0\text{--}900\text{ cm}^{-1}$ region have been observed.²³ In view of the smaller number of normal modes in hexatriene we would therefore have expected to see at most the same number of bands and not more. That we in fact see more points to changes in the geometry of *cis*-hexatriene in the 2^1A_g state in which these low frequency modes are involved to a larger extent than in other unsubstituted polyenes.

Inspection of Table I shows that positions of many of the combination bands associated with the low frequency vibrations are shifted from what would be expected under the harmonic approximation. While the bandwidths do increase with increasing excitation energy, this can at most account for part of the shift. We believe that anharmonicity of the potential energy surface of the 2^1A_g state is primarily responsible for these deviations.

E. Fine structure

Up till this point we have been concerned with the general aspects of the $1^1A_g \rightarrow 2^1A_g$ excitation spectrum. Although this study has been the first one in which the $1^1A_g \rightarrow 2^1A_g$ transition in an unsubstituted polyene has been studied in the gas phase, the qualitative picture obtained from these considerations agrees well with that derived from previous studies on unsubstituted polyenes in the solid phase and substituted polyenes in the gas and solid phase: the 2^1A_g state is below the 1B_u state, vibronic progressions mainly involve the symmetric C=C and C-C stretch vibrations and the frequency of these two stretch vibrations is larger in the 2^1A_g state than in the ground state. We now wish to look into more detail at the ways in which the 2^1A_g state of hexatriene differs from the general picture of the polyene 2^1A_g state.

1. The doubled origin

Most intriguingly the origin of the $1^1A_g \rightarrow 2^1A_g$ excitation spectrum is not a single band but consists of a feature

that comprises two bands separated by 5 cm^{-1} . From the reasoning given below and from the results of *ab initio* calculations that will be discussed later it will become clear that we have to conclude that *cis*-hexatriene in the 2^1A_g state is not planar as it is in the ground state,²¹ but distorts to at least two distinct nonplanar geometries.

It could be argued that the lowest energy component is actually a hot band. This possibility can be ruled out on experimental as well as theoretical grounds. Changing the backing pressure of the helium over a range from 1 to 100 psi did not influence the ratio of the intensities of the two origin bands. Moreover, in general hot bands have a significantly larger bandwidth: the bandwidths of the two components of the origin are approximately equal. Finally, if the first band were a hot band it would be reasonable to expect more hot bands since its intensity is relatively large (about 50% of the intensity of the second band).

Another possible reason for the split origin could be that the low energy band is the 0-0 transition and the band at 5 cm^{-1} a very low energy torsional vibration. In this case, however, a long progression in this vibration would have been expected.

Finally, we have to consider the possibility that the two bands arise from two types of *cis*-hexatriene molecules in the ground state, these two types being either single bond conformers of *cis*-hexatriene or two nonplanar molecules, distorted from planarity along two different vibrational coordinates. With respect to the second possibility previous experimental studies have shown that it is very unlikely that *cis*-hexatriene is nonplanar in the ground state.²¹ Moreover, for both possibilities given above the intensity ratio of the two origin bands would be expected to depend on the reservoir temperature of the sample. Changing the reservoir temperature from 0 to 25°C did not influence this ratio.

All of the above considerations point to changes in the molecular geometry in the 2^1A_g state as being responsible for the presence of the two origin bands. The observation that the two components of the origin band represent the bands of largest intensity in the spectrum and the conclusion that the electronic structure of the 2^1A_g state in *cis*-hexatriene is not qualitatively different from that observed for other polyenes indicates that these geometry changes are relatively small.

2. Vibronic band profiles

A more detailed consideration of the low-frequency region of the excitation spectrum of Fig. 2 reveals that many of the vibrational bands exhibit a multiplet structure (see Fig. 4). As the excitation energy increases we observe that this multiplet structure gradually disappears. The last band clearly exhibiting the multiplet structure is located at 360 cm^{-1} , though above this energy the envelope width of the resonance lines increases to about 13 cm^{-1} . This increase in bandwidth could in part be due to the multiplet structure being hidden within the line.

An explanation for the multiplet structure is not easily given. We first note that this structure indeed must derive from the splitting of one band into more bands and not from

several individual bands which are accidentally quasidegenerate since the number of observed bands is incompatible with the possible number of low-frequency vibrations. Furthermore, we note that the multiplet structure is unlikely to derive from the two conformers present in the 2^1A_g state since in that case a splitting into two with an intensity ratio that should more or less resemble the origin intensity ratio is expected. We observe on the contrary for the majority of the vibrations a pattern that suggests a splitting into three.

One of the possible explanations for the multiplet structure could be looked for in the quasidegeneracy of the torsional levels along which the molecule is distorted in the 2^1A_g state. On the potential energy surface of the 2^1A_g state of *cis*-hexatriene two double minimum potentials are present. For each of these two double minimum potentials the torsional levels exhibit a quadruple degeneracy. If this degeneracy would be lifted it is clear that a multiplet structure could result. The condition for such a destroying of degeneracy lies in the amount of tunneling through the barrier dividing the two minima, which would imply that the potential for *cis*-hexatriene along these torsional coordinates is very shallow.

The apparent splitting into three suggests the presence of three conformers in the 2^1A_g state. Recent calculations by Zerbetto and Zgierski²⁴ have shown that *trans*-butadiene in the 2^1A_g state has three nonplanar conformers though our calculations (see below) suggest that in *cis*-hexatriene only two nonplanar conformers are present. From an experimental point of view, an additional problem with this explanation would be that the excitation spectrum seems to reveal only two origins with equal widths limited by the laser bandwidth. This, in turn, implies that two of the conformers would have their origins within less than 1 cm^{-1} if indeed

three conformers were present. It is clear that a final answer to the origin of the multiplet structure would greatly benefit from a study with higher resolution.

F. Experiments on *trans*-hexatriene

The results given above apply to the *cis*-isomer of hexatriene. In this study we have also tried to apply the same REMPI techniques to investigate the electronic properties of the *trans*-isomer. In the excitation spectrum of this isomer features have been observed with a much smaller signal to noise ratio and with a seemingly larger bandwidth than in *cis*-hexatriene. These features are located below the origin of the $1^1A_g \rightarrow 2^1A_g$ transition of *cis*-hexatriene, which at first suggested to us that the origin for the *trans*-isomer was below that of the *cis*-isomer. Studies on octatetraene have shown that in the condensed phase the 2^1A_g state of the *trans-trans*-isomer has a slightly higher excitation energy than that of the *cis-trans*-isomer (187 cm^{-1} in *n*-octane).^{5,22} The larger transition dipole for the 2^1A_g state in the *cis*-isomer would imply a larger gas to solution shift which could account for the reversed order of excitation energies in the gas phase, but there is also the possibility that the features observed for the *trans*-isomer arise from within the ionization continuum and not from the 2^1A_g state. A definitive resolution of the proper assignment of bands seen for the *trans*-isomer waits on improvement of our signal to noise ratio.

To verify that difficulty in observing resonances for the *trans*-isomer indeed has to do with the electronic properties of the 2^1A_g state of this isomer and is not due to a higher ionization threshold, we have located the lowest energy ionization threshold for both isomers. In Fig. 5 this region is depicted for the *cis*-isomer and the *trans*-isomer. Figure 5

FIG. 5. Ionization threshold region for the *cis*- and *trans*-isomers of hexatriene. Since this region is reached by a direct two-photon absorption the actual energy scale is twice the energy of the photons.

shows that there is a difference between the ionization thresholds for the two isomers: for the *cis*-isomer the ionization threshold is $2 \times 33\,460 = 66\,920 \pm 5 \text{ cm}^{-1}$, for the *trans*-isomer at $2 \times 33\,305 = 66\,610 \pm 5 \text{ cm}^{-1}$. Since the photoionization threshold depends on the magnitude of the local electric field these numbers may be as much as $100\text{--}200 \text{ cm}^{-1}$ different from the absolute ionization thresholds.²⁵ They agree, however, very well with previous, though less accurate, results.²⁶

In *cis*-hexatriene and *trans*-hexatriene the $1^1A_g \rightarrow 2^1A_g$ transition is electronically forbidden. The observation that, despite this forbidden character in both isomers, resonance enhancement is observed for the *cis*-isomer and not for the *trans*-isomer underlines the importance of the symmetry properties. Additionally, the fact that the absorption cross section for the 2^1A_g state is so much lower for the *trans*-isomer supports the conclusion that the distortion from planarity in the 2^1A_g state is not very large since it is not to be expected that such a distortion is principally different in the two isomers. In other words, if the distortion from planarity in the *trans*-isomer were large enough to significantly affect the inversion symmetry we would have expected to also observe signals from the 2^1A_g state of the *trans*-isomer. We conclude that to a good approximation the *trans*-isomer still has inversion symmetry in the 2^1A_g state.

With this conclusion in mind it seemed to us that a better approach for the *trans*-isomer would be to do a $2h\nu_1 + h\nu_2$ resonance enhanced ionization study. In this scheme, two photons of energy $h\nu_1$ are used to excite the molecule to the 2^1A_g state while one photon of energy $h\nu_2$ is used to make the transition from the 2^1A_g state to the ionization continuum. A crucial condition that must be met in such a study is that ionization signals from only ν_1 or only ν_2 must be smaller or at most of the same order of magnitude as the signals arising from the $2 + 1$ process. In our initial attempt at a two-color three-photon ionization experiment, an excimer laser operated with ArF (193 nm) or XeCl (308 nm) was used to generate ν_2 . The power of this laser was adjusted to such a level that negligible contributions from higher order processes occurred. Under these conditions, however, we failed to observe any $2 + 1$ process for either wavelength (193 or 308 nm). The use of 193 nm is compromised by the presence of a state in this energy region which enhances a $1 + 1$ ionization process; 308 nm fails because at 154 nm a state is present which enhances a $2 + 1$ ionization process.

IV. THEORETICAL CALCULATIONS

In this section we will discuss some preliminary results of *ab initio* calculations that we have performed in order to investigate the experimental conclusion that *cis*-hexatriene is distorted from planarity in the 2^1A_g state. These calculations will be described in more detail elsewhere; here we wish to focus on their main conclusions and link their results with the experimental results.

The *ab initio* calculations were performed using the complete active space self-consistent field (CASSCF) approach for the π -electron space, i.e., all possible configura-

tions (175), arising from assigning the 6 π electrons in *cis*-hexatriene to 6 π orbitals, were used to expand the electronic wave function. The basis employed initially was the STO-3G basis, which recent calculations on *trans*-butadiene and *trans*-hexatriene have shown to be capable of satisfactorily reproducing the main characteristics of the 2^1A_g state.^{22,24} Additional calculations were performed using the double zeta (DZ) basis described in Ref. 27 in order to determine the dependence of our results on the basis. Geometry optimizations and calculations of force fields have been performed using the GAMESS program developed by Dupuis *et al.*²⁸

In the following we will first discuss the results obtained with the STO-3G basis after which these results will be compared with the calculations using the DZ basis.

Geometry optimization of the ground state of *cis*-hexatriene leads to a planar structure of C_{2v} symmetry in accordance with our and previous²¹ experimental conclusions that the two conformers observed in the $1^1A_g \rightarrow 2^1A_g$ excitation spectrum do not arise from distortions in the ground state. The optimization of the 2^1A_g state within C_{2v} symmetry and the subsequent calculation of vibrational frequencies resulted, however, in the presence of two imaginary frequencies indicating an instability of the molecule with respect to these two vibrational coordinates. Similar results have also been obtained in recent calculations performed on the 2^1A_g state of *trans*-hexatriene, though a search for the stable configuration(s) was not performed.²² Such a search for the 2^1A_g state of *cis*-hexatriene results in the location of two stable minima, one of C_2 symmetry and one of C_s symmetry. Calculation of the force fields for both configurations confirmed that both are stable minima since in these configurations all frequencies are real. These two minima are virtually degenerate in agreement with the experiment: the C_2 configuration is stabilized with respect to the optimized C_{2v} configuration by 241 cm^{-1} , the C_s configuration by 244 cm^{-1} .

In Fig. 6 these two stable configurations for the 2^1A_g state are depicted. From this figure it is seen that the 2^1A_g state of hexatriene is stabilized by an out of plane deformation of the terminal hydrogen atoms which are about 10 and 20° out of the molecular plane. The rest of the molecule is to a good approximation still planar and has responded to the excitation from the ground state by merely changing the bond lengths within the carbon skeleton.

These results change dramatically upon changing the

FIG. 6. Calculated stable configurations of *cis*-hexatriene in the 2^1A_g state using an STO-3G basis. The left part of the picture shows the configuration of C_s symmetry, the right part the configuration of C_2 symmetry.

basis to the DZ basis. When this basis is used the calculations predict that the C_{2v} configuration is stable in both the ground state as well as in the 2^1A_g state. Calculation of the energy of the 2^1A_g state in the configurations in which the terminal hydrogen atoms are taken out of the molecular plane in a similar way as found before with the STO-3G basis reveals that these geometries are only 5 cm^{-1} higher in energy than the C_{2v} configuration. This demonstrates that, even though the C_{2v} geometry is a stable minimum, the molecule is extremely flexible with respect to out of plane distortions of the terminal hydrogen atoms. It may well be that on the energy scale involved in the present calculation σ - σ and σ - π correlation effects are no longer negligible and should also be considered in order to come to a reliable prediction concerning the stable geometry of *cis*-hexatriene in the 2^1A_g state.

Our experimental results show that *cis*-hexatriene in the 2^1A_g state is distorted to two different conformers though from an electronic point of view we have concluded that this distortion is not very large. Our *ab initio* calculations are in part in agreement with this conclusion. Though they do not confirm unambiguously a distortion it is clear that the molecule is at least extremely floppy at its terminal carbon atoms. Since experimentally a distortion has been observed we conclude that the stabilization energy predicted by the STO-3G calculation is a higher limit of the real stabilization energy. This in turn implies that the molecule in the 2^1A_g state is not confined to one distorted configuration or the other but a significant tunneling through the barrier formed by the C_{2v} configuration is likely to occur.

Finally, it is worthwhile to consider the present experimental and theoretical results in the context of results obtained for other linear polyenes. Recently, Zerbetto and Zgierski reported on calculations on the 2^1A_g state of *trans*-butadiene.²⁴ It was found that the molecule in the 2^1A_g state is also distorted: three nonplanar configurations were calculated to be stable minima on the potential energy surface. Though qualitatively the kind of distortion present in *trans*-butadiene is similar to the one found here for *cis*-hexatriene, the sizes of the distortions from planarity and the stabilization energies are significantly different. Rotations up to 50 deg are present in *trans*-butadiene, while the stabilization energy of all three conformers is about 1650 cm^{-1} with both an STO-3G and 4-31G basis. On the other hand, for octatetraene it has recently been calculated that the 2^1A_g state is planar,²² in accordance with previous experimental results of studies of octatetraene in the solid phase.⁵ Hexatriene, therefore, seems to be a molecule which is intermediate between butadiene and octatetraene, both in size of distortion as well as stabilization energy. In this respect it is gratifying to find that our calculations indicate that hexatriene is indeed a borderline case between stable and unstable configurations in the 2^1A_g state.

One of the conclusions of the calculations on butadiene was that the nonplanarity of the 2^1A_g state leads to a strong increase of the rate of radiationless decay to the ground state explaining the absence of fluorescence in butadiene. In hexatriene we have experimentally observed that the molecule is distorted in the 2^1A_g state, thereby clearly meeting the requirements for the enhancement of radiationless decay by

out-of-plane modes to work. This could account for the apparent absence of fluorescence in hexatriene.

V. CONCLUSIONS

The application of resonance enhanced multiphoton ionization spectroscopy has enabled us to observe for the first time vibrationally resolved spectra of the 2^1A_g state of an unsubstituted polyene in the gas phase. In most aspects the electronic structure of the 2^1A_g state of *cis*-hexatriene has been found to agree well with current theories on the electronic structure of polyenes: the 2^1A_g state is below the 1B_u state and vibrational progressions are mainly based on the symmetric C=C stretch vibration. In addition to the C=C stretch vibration notable vibrational activity has been observed in the low-energy torsional and bending modes. This increase in activity with respect to the *trans*-polyenes has been attributed to the different symmetry properties of *cis*-hexatriene and significant geometry changes in the 2^1A_g state. The excitation spectrum has shown that in one aspect the 2^1A_g state of *cis*-hexatriene is markedly different from that of the polyenes studied up till now. The presence of two origin lines separated by 5 cm^{-1} can only be interpreted as arising from two nonplanar configurations in the 2^1A_g state. *Ab initio* calculations indicate that this distortion from planarity is mainly located at the terminal hydrogen atoms. From our experiments on *cis*-hexatriene and additional experiments on *trans*-hexatriene it has to be concluded, however, that the distortion is not very large.

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