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The 2 ^1A_g state of isolated *cis,trans*-1,3,5,7-octatetraene: Two-color resonance enhanced two-photon ionization studies

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Vibrationally resolved 1 $^1A_g \rightarrow 2\ ^1A_g$ excitation spectra and decay times for *cis,trans*-1,3,5,7-octatetraene seeded in a supersonic He expansion have been measured by two-color resonance enhanced two-photon ionization spectroscopy. The excitation energy of the 1 $^1A_g \rightarrow 2\ ^1A_g$ 0–0 band (29 035 cm^{-1}) is $\sim$6500 cm^{-1} lower than the 35 484 cm^{-1} excitation energy of the 1 $^1A_g \rightarrow 1\ ^1B_u$ 0–0 band. The intensity pattern of the vibronic development of this spectrum is qualitatively similar to the pattern observed previously in solid state experiments. However, a detailed analysis of the vibrational structure reveals that the electronic structure of the 2 ^1A_g state is more susceptible to external perturbation than previously suspected. The decay times measured for vibronic levels in the 2 ^1A_g state decrease with increasing vibrational energy, most dramatically for vibrational energies 1200 cm^{-1} and higher. This indicates the increasing importance of a nonradiative decay channel which is most reasonably associated, at least in part, with *cis-trans* isomerization in the 2 ^1A_g state.

I. INTRODUCTION

The study of linear polyenes is in part motivated by their occurrence as chromophores in biological complexes. In order to obtain a very basic understanding of the photophysical and photochemical processes that take place in these biological systems, it is crucially important to elucidate the electronic characteristics of polyene chromophores.[1] In this respect 1,3,5,7-octatetraene (henceforth called octatetraene) can be considered to be a paradigm linear polyene in that much of the detailed knowledge of polyene electronic structure that we now have has come from studies on octatetraene isomers and derivatives.

For example, the discovery that the lowest energy excited singlet state in most linear polyenes is not the strongly allowed 1 ^1B_u state as predicted by molecular orbital theory at the Hartree–Fock level followed from the observation of a lower energy dipole forbidden state in 1,8-diphenyl-1,3,5,7-octatetraene.[2,3] Theoretical studies showed that electron–electron interaction significantly mixed singly and doubly excited A_g configurations leading to a low energy highly correlated 2 ^1A_g state.[4] The proof of the strict validity of this symmetry label was established by high resolution one and two-photon excitation and emission spectroscopy on *trans,trans*-octatetraene in *n*-octane at liquid helium temperatures.[5] Subsequent studies on various isomers and conformers of octatetraene[6–11] demonstrated the, in many ways unusual, photochemical and photophysical properties of the 2 ^1A_g state of linear polyenes. These include the bond order reversal that takes place upon excitation from the ground state into the 2 ^1A_g state, the fact that *cis-trans* isomerization proceeds adiabatically over relatively low barriers in the 2 ^1A_g state, and the increase in C=C stretch frequency on excitation to the 2 ^1A_g state (a property of the 2 ^1A_g state that may be explained in terms of vibronic mixing of the ground and 2 ^1A_g states[12]).

Unsubstituted linear polyenes have relatively low quantum yields for fluorescence and are quite reactive. Because of this, the studies cited above as well as experiments on a number of longer unsubstituted polyenes have been performed on molecules dissolved in alkanes at low temperatures, that is, under nonisolated conditions. Attempts to observe the 2 ^1A_g state of these polyenes in the gas phase by fluorescence detection were always compromised by degradation of the samples by polymerization and other reactions. Though the relative position and potential energy surface of the 2 ^1A_g state are not expected to be dramatically different in the absence of solvent interactions, it is nonetheless very important to be able to study polyenes under strictly isolated conditions in order to obtain the unperturbed electronic structure and to quantitatively assess the effects of external perturbations.

Recently we have demonstrated that resonance enhanced multiphoton ionization spectroscopy with mass selective ion detection is a powerful tool to study polyenes in supersonic jet expansions.[13–15] Using this technique we were able to directly observe the 2 ^1A_g state of hexatriene,[13,14] thereby realizing a long outstanding experimental goal. The subsequent investigation of various isomers of alkyl substituted hexatrienes[15] by the same technique allowed us to greatly expand our knowledge of the dependence of the triene 2 ^1A_g state on alkyl substitution and molecular geometry.

In this paper we report the first observation of the 2 ^1A_g state of isolated octatetraene. By measuring the wavelength dependence of parent ion yields for two-color two-photon ionization of octatetraene seeded into a supersonic He expansion we have obtained a fully resolved 1 $^1A_g \rightarrow 2\ ^1A_g$ excitation spectrum. Analysis of this spectrum shows that it is the spectrum of the *cis,trans* isomer of octatetraene, even

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though the isomer distribution in the reservoir must have a *trans,trans* to *cis,trans* ratio of ~4. The fact that the cross section for the 1 $^1A_g \rightarrow 2\ ^1A_g$ transition in the *trans,trans* isomer is too small to be detected under our experimental conditions is consistent with our previous inability to detect the 2 ^1A_g state in *trans*-hexatriene[13,14] (although the symmetry labels A_g and B_u are not correct for *cis,trans* polyenes, we use these C_{2h} symmetry labels to emphasize that, except for geometry, there is a close correspondence between the states in the *trans,trans* and *cis,trans* isomers). Comparison of the present results to spectra measured for low temperature *n*-alkane solutions allows us to determine how the electronic structure of the 2 ^1A_g state is influenced by crystal fields and molecular geometry. Measurement of the lifetimes of various vibronic levels in the 2 ^1A_g state leads us to the conclusion that nonradiative decay processes, presumably including *cis-trans* isomerization, are strongly enhanced at vibronic energies ~1200 cm^{-1} above the 2 ^1A_g zero point level. Finally, analysis of the present results together with our previously reported spectra of hexatriene gives some insight into what can in general be expected for the one-photon excitation of the 2 ^1A_g state of *all-trans* polyenes.

II. EXPERIMENTAL

1,3,5,7-octatetraene has been synthesized using the procedure of Spangler and Little.[16] Following synthesis, octatetraene was stored at − 10 °C as a dilute solution in *n*-pentane. The sample used in the experiments was prepared by transferring part of the stock solution into a glass tube and evaporating most of the *n*-pentane by bubbling argon through the solution. Gas chromatography together with mass spectrometry (GC/MS) and nuclear magnetic resonance (NMR) analysis showed that the sample contained the *trans,trans* and *cis,trans* isomers in the ratio of 4:1.

A detailed description of our experimental setup for multiphoton ionization spectroscopy has been given elsewhere.[14] The only change in the apparatus involves the pumps: now the main chamber is pumped by an Edwards ETP10/1000 turbomolecular pump (1400 ℓ/s) and the mass spectrometer chamber is pumped by a Varian Turbo-V200 turbomolecular pump (170 ℓ/s). With this pumping system we reach a pressure of 10^{-6} Torr in the main chamber and 10^{-7} Torr in the mass spectrometer chamber.

These experiments are based on the one-color resonance enhanced multiphoton ionization experiments described before[14] in which the optical excitation is provided by the frequency doubled output of a Spectra Physics PDL-2 dye laser pumped by a DCR-3 Nd:YAG laser. This laser beam is focused into the excitation region between the ion acceleration plates of the mass spectrometer by a 20 cm focal length lens where it intersects at right angles the molecular beam created by a pulsed valve (R. M. Jordan Co.) with a 0.5 mm diam nozzle connected to the sample reservoir containing octatetraene and 3 atmospheres He at room temperature. Ions generated by the excitation beam are accelerated through a time-of-flight mass spectrometer (R. M. Jordan Co.) and detected by a dual microchannel plate (Galileo Electrooptic Corp.). The ion signal is amplified by a fast preamplifier (Stanford Research SR240) and the mass peak of the molecular ion is selected and averaged using standard boxcar techniques.

For the two-color resonance enhanced multiphoton ionization experiments the second color was supplied by an excimer laser (Lambda Physik LPX105i) operating on ArF (193 nm). In our configuration the excimer laser beam travels in the opposite direction to the tunable laser beam and is not focused but merely reduced in size by a diaphragm to a beam cross section of 1 cm × 0.5 cm. Temporal overlap of the two laser beams is achieved by a Bradley 176B pulse generator. After being triggered by the oscillator sync output of the Nd:YAG laser, this system triggers independently both the Q-switch of the Nd:YAG laser as well as the excimer laser.

The lifetime of a resonance was determined by changing the delay between the two laser pulses while monitoring the ion signal at the mass peak of the molecular ion.

In the two-color experiments the intensities of both the excitation beam from the Nd:YAG system and the ionization beam from the excimer laser were reduced to such an extent that the number of ions generated by either laser alone was at least two orders of magnitude smaller than the number of ions generated by both lasers at the most intense resonance. In practice this meant that the excimer laser energy was set to ~20 mJ/pulse while the tunable laser could be run at full power.

In recording the excitation spectra the dye laser was scanned in steps of 0.05 or 0.1 Å for the 1 $^1A_g \rightarrow 2\ ^1A_g$ transition and 0.2 Å for the 1 $^1A_g \rightarrow 1\ ^1B_u$ transition. In both cases the ion signal was averaged for 8 s/point.

III. RESULTS

The 1 $^1A_g \rightarrow 2\ ^1A_g$ excitation spectrum of octatetraene as measured by two-color resonance enhanced two-photon ionization spectroscopy is shown in Fig. 1. Positions and assignments of the major bands in this spectrum are summarized in Table I. The spectrum in Fig. 1 has been constructed by

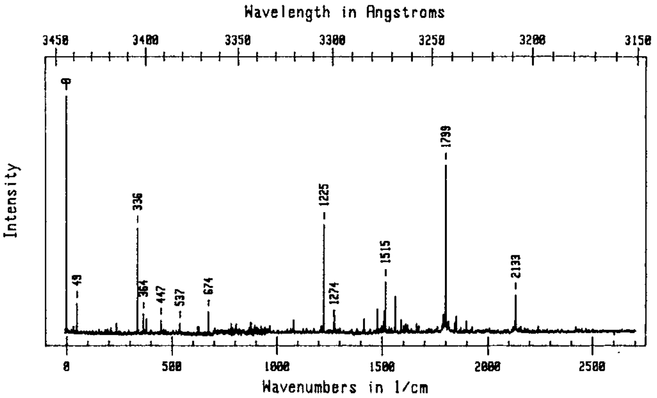

FIG. 1. 1 $^1A_g \rightarrow 2\ ^1A_g$ excitation profile for resonance enhanced two-color two-photon photoionization of *cis,trans*-octatetraene seeded in a supersonic He expansion. Intensity (vertical axis) is the relative number of ions at the octatetraene molecular mass and wavelength (horizontal axis) is the wavelength of the tunable dye laser photons that, together with 193 nm photons, gave molecular ions.

TABLE I. Vibrational analysis of the bands of intensity larger than 4% of the intensity of the 0–0 transition in the 1 $^1A_g \rightarrow 2\ ^1A_g$ excitation spectrum of *cis,trans*-octatetraene.

Wave number frequency (cm^{-1})[a]	Assignment	Intensity	Deviation from harmonic approximation (cm^{-1})
0	0–0	100	...
33	ν_1	4	...
49	ν_2	14	...
210	ν_3	4	...
236	ν_4	5	...
336	ν_5	45	...
364	ν_6	9	...
379	$\nu_5 + \nu_2$	7	−6
448	ν_7	7	...
538	ν_8	5	...
623	ν_9	4	...
628	ν_{10}	4	...
674	$2\nu_5$	10	+2
783	$\nu_7 + \nu_5$	5	+1
807	$\nu_7 + \nu_6$	5	−5
876	$\nu_8 + \nu_5$	6	+2
896	$2\nu_7$	4	0
968	ν_{11}	4	...
1080	ν_{12}	7	...
1213	$\nu_8 + \nu_5 + \nu_5$	4	+3
1226	$\nu_{13} = \nu_{C-C}$	46	
1275	$\nu_{13} + \nu_2$	6	0
1416	$\nu_{12} + \nu_5$	7	0
1479	ν_{14}	11	...
1499	ν_{15}	5	...
1509	ν_{16}	10	...
1516	ν_{17}	23	...
1563	$\nu_{13} + \nu_5$	17	+1
1589	$\nu_{13} + \nu_6$	7	−1
1611	$\nu_{13} + \nu_5 + \nu_2$	5	0
1616	$\nu_{12} + \nu_8$	4	−2
1621	ν_{18}	5	...
1662	ν_{19}	5	
1673	$\nu_{13} + \nu_7$	4	−1
1761	$\nu_{13} + \nu_8$	4	−3
1783	$\nu_{12} + \nu_6 + \nu_5$	5	−3
1789	ν_{20}	9	...
1799	$\nu_{21} = \nu_{C-C}$	71	...
1814	$\nu_{14} + \nu_5$	6	−1
1845	$\nu_{16} + \nu_5$	6	0
1850	$\nu_{17} + \nu_5$	8	−2
	$\nu_{21} + \nu_2$	...	+2
1899	$\nu_{13} + \nu_5 + \nu_5$	7	+1
1927	$\nu_{14} + \nu_7$	4	0
	$\nu_{13} + \nu_6 + \nu_5$	...	+1
2122	$\nu_{20} + \nu_5$	4	−3
2134	$\nu_{21} + \nu_5$	17	−1
2243	$\nu_{21} + \nu_7$	4	−4
3583[b]	$2\nu_{21}$	...	−15

[a] Frequency in cm^{-1} with respect to 0–0 transition located at 29 035 cm^{-1}.
[b] Not shown in Fig. 1.

linking three consecutive scans. To link two scans, one of the scans is linearly scaled so as to give a best fit in the least-squares sense to the other scan in the region where the two scans overlap. Separate measurements of the intensities of the more intense peaks in the spectrum under identical conditions of excitation power has confirmed the correctness of the relative intensities of the bands in Fig. 1. In the region 800–1000 cm^{-1} above the lowest energy band a decrease in the signal to noise ratio is evident. This decrease is due to the fact that in this region we are working at the edges of both of the dye gain curves of the two scans (DCM and LDS698).

The lowest energy ionization potential of octatetraene has been located at ~7.8 eV (Ref. 17) which would imply that one-color resonance enhanced two-photon ionization is only possible at photon energies higher than 31 455 cm^{-1} (3179 Å). Indeed we have not been able to observe any resonance enhancement by using only one color which proves that the spectrum in Fig. 1 should be assigned to the 2 ^1A_g state and not to a state reached by two-photon excitation. If the latter were the case, the overall ionization process would have been a three-photon ionization which would also have been possible to achieve in this energy region by the use of only one color.

The lifetimes of several bands in the 1 $^1A_g \rightarrow 2\ ^1A_g$ excitation spectrum are given in Table II and plotted in Fig. 2. These lifetimes have been determined by monitoring the molecular ion signal as a function of the time delay between the excitation and ionization laser pulses and fitting the resulting decay curve by the convolution of a Gaussian laser pulse with an exponential decay. In the fits five parameters were varied: the background level, the time at which the two laser pulses coincide in time, the width of the Gaussian, the amplitude of the Gaussian, and the exponential decay time. Figure 3 shows typical lifetime data and the fitted curves. For some of the weaker bands it was not possible to determine all five of the above-mentioned parameters. In those cases the Gaus-

TABLE II. Lifetimes of vibronic levels as a function of excess vibrational energy.

Wave number frequency (cm^{-1})[a]	Decay time (ns)
0	273
49	244
236	259
336	280
364	266
1080	226
1226	254
1416	206
1479	169
1516	160
1563	157
1799	112
1850	119
1899	119
2134	53
2243	28

[a] Energy in cm^{-1} with respect to 0–0 transition located at 29 035 cm^{-1}.

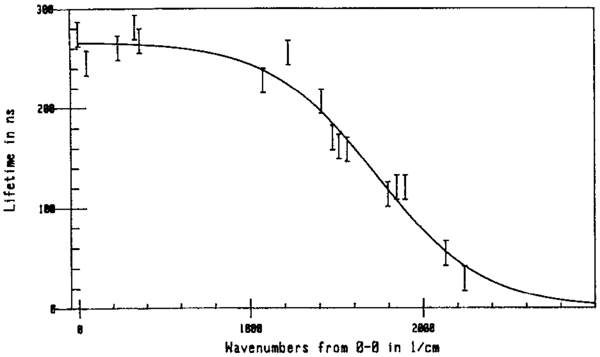

FIG. 2. Vibronic level decay times vs 2 ^1A_g vibronic energy. The smooth curve is the threshold law profile with $1/\tau = 1/\tau_0 + \nu_A e^{-\Delta E/kT}$, $\tau_0 = 267$ ns, $\nu_A = 13.5 \times 10^3\ \mathrm{s}^{-1}$ and $\Delta E/hC = 307\ \mathrm{cm}^{-1}$.

sian width was fixed at 12 ns which was the mean value of the widths determined in the fits in which the width was varied.

Finally, Fig. 4 shows the excitation spectrum measured near the 0–0 band of the 1 $^1A_g \rightarrow 1\ ^1B_u$ transition. The spectrum in Fig. 4 has been recorded using the two-color techniques described above. A similar spectrum, albeit with a considerably smaller signal to noise ratio, has been obtained using only one color. In both experiments the intensity of the excitation beam had to be attenuated by a factor of 200 with respect to the experiments on the 2 ^1A_g state in order to avoid saturation. The observation that we obtain a better signal to noise ratio in the two-color experiment indicates that the cross section for the ionization step is considerably less than the cross section for excitation to the 1 ^1B_u state.

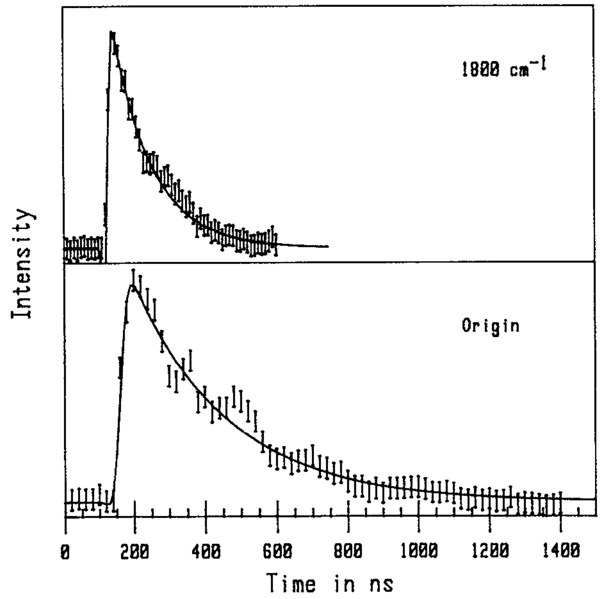

FIG. 3. Examples of 2 ^1A_g vibronic level decay data for *cis,trans*-octatetraene seeded into a supersonic He expansion. The data points are for excitation at the 0–0 band (lower panel) and 1800 cm^{-1} above the 0–0 band (upper panel). The smooth curves are the best fit profiles assuming the convolution of an exponential decay with a Gaussian driving pulse.

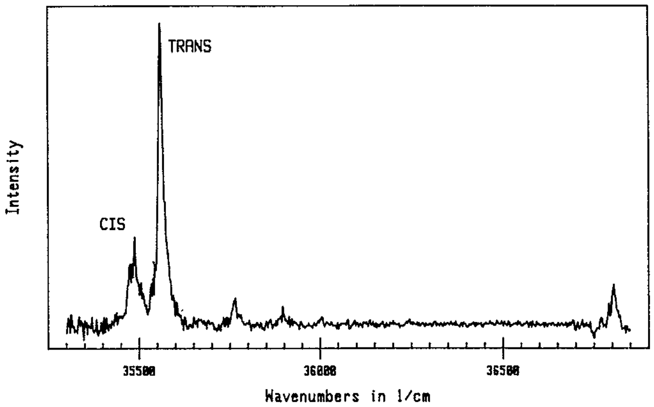

FIG. 4. Origin region of the 1 $^1A_g \rightarrow 1\ ^1B_u$ excitation profile for resonance enhanced two-color two-photon photoionization of octatetraene seeded in a supersonic He expansion.

IV. DISCUSSION

A. Assignment to the *cis,trans* isomer

Since the octatetraene was an isomeric mixture, the first question that has to be resolved is whether Fig. 1 contains bands from the spectra of both or just one of the double bond isomers. If these spectra derive from just one isomer, is it *trans,trans* or *cis,trans* octatetraene? Our previous studies on the 2 ^1A_g state of hexatriene[13,14] and alkyl substituted hexatrienes[15] have shown the caution that one is obliged to take in the assignment of the 1 $^1A_g \rightarrow 2\ ^1A_g$ excitation spectra to specific isomers. For hexatriene where we were able to obtain pure *cis* and *trans* samples, we found that our present sensitivity only allowed the detection of the 1 $^1A_g \rightarrow 2\ ^1A_g$ excitation for the noncentrosymmetric *cis* isomer. Similar results were obtained for heptatriene (1-methyl hexatriene): we could only detect 2 ^1A_g excitation for isomers that contained at least one *cis* double bond. Further, for heptatriene where there are two distinguishable double bonds, we found that the 1 $^1A_g \rightarrow 2\ ^1A_g$ transition dipole significantly increased with the number of *cis* double bonds, that is, the transition moment for *Z,Z*-heptatriene is larger than that for *Z,E* or *E,Z*-heptatriene. In consequence, the intensities observed in a 1 $^1A_g \rightarrow 2\ ^1A_g$ excitation spectrum of a mixture does not in any way reflect the isomeric composition of that sample. Thus, even though GC/MS analysis showed that the isomeric composition of our sample was 4:1 *trans,trans*:*cis,trans*, our experience with hexatriene and heptatriene suggests that we should only be able to see the spectrum of the *cis,trans* isomer. This is confirmed by a number of lines of argument based on the comparison of our spectra to the high resolution spectra measured for *cis,trans*- and *trans,trans*-octatetraene in the solid state.

It is clear from the spectroscopy of octatetraene in low temperature *n*-alkane crystals that, in the absence of severe environmental perturbations, the dipole strength of the 1 $^1A_g \rightarrow 2\ ^1A_g$ transition of the *cis,trans* isomer is enormously larger than that of the *trans,trans* isomer. One and two-photon spectroscopy on octatetraene in *n*-octane at 4.2 K has unambiguously proven that *trans,trans*-octatetraene retains

C_{2h} symmetry upon excitation into the 2 ^1A_g state.[5] Consequently, the 1 $^1A_g \rightarrow 2\ ^1A_g$ transition is not only electronically forbidden to the extent that the 2 ^1A_g state is doubly excited, but is also symmetry forbidden. In the one-photon excitation spectrum the 0–0 of the 1 $^1A_g \rightarrow 2\ ^1A_g$ transition is not seen: the fluorescence excitation spectrum is built on four false origins based on b_u symmetry vibrations.[5] These b_u symmetry vibrations are not seen in the spectrum shown in Fig. 1.

Although subsequent studies on *trans,trans*-octatetraene in other *n*-alkanes demonstrated that the strict centrosymmetry observed in *n*-octane is relatively easily broken,[18] only in *n*-hexane where the matrix perturbation is expected to be extremely strong does the excitation spectrum have the appearance of a symmetry allowed transition. In *n*-heptane, *n*-nonane, and *n*-decane, even though the 0–0 transition is observed, it is significantly weaker than the vibronically induced false origins. In stark contrast, though the vibronic coupling is still present, these promoting modes are so weak relative to the symmetry allowed bands in the 1 $^1A_g \rightarrow 2\ ^1A_g$ spectrum of the *cis,trans* isomer in *n*-octane that they cannot be seen.[9] This means that the relaxation of the symmetry selection rule in the case of the *cis,trans* isomer leads to a dipole strength of the 1 $^1A_g \rightarrow 2\ ^1A_g$ transition that is at least two orders of magnitude larger than that of the *trans,trans* isomer. Thus, for a sample that is a 4:1 *trans,trans*:*cis,trans* mixture the intensity 1 $^1A_g \rightarrow 2\ ^1A_g$ spectrum for the *cis,trans* isomer is expected to be at least 20 times that of the *trans,trans* isomer. This means that all of the intense bands in the spectrum shown in Fig. 1 should be assigned to *cis,trans* octatetraene.

This intensity argument is buttressed by our inability in the case of *trans*-hexatriene to detect resonance enhancement of the ion signal by the 2 ^1A_g state. The solid state experiments establish that in a symmetric environment dipole intensity for the 1 $^1A_g \rightarrow 2\ ^1A_g$ transition in *trans,trans*-octatetraene derives from vibronic coupling of the 2 ^1A_g and 1 ^1B_u states. This intensity borrowing seems to be quite general for *all-trans* polyenes. In the supersonic jet experiments on 1,4-diphenyl butadiene[19] and 1,6-diphenyl hexatriene[20] and the low temperature experiments on 2,10-dimethyl undecapentaene in nonane[21] and decatetraene in undecane[22] the 2 ^1A_g excitation spectrum is mainly built on false origins. The reasonable expectation then is that *trans*-hexatriene also derives its 1 $^1A_g \rightarrow 2\ ^1A_g$ transition dipole from 2 ^1A_g–1 ^1B_u vibronic coupling. For hexatriene we have measured a 2 ^1A_g–1 ^1B_u energy gap of 5270 cm^{-1}, while on the basis of the present experiments the analogous gap in octatetraene is 6515 cm^{-1}, 1245 cm^{-1} larger than hexatriene. If the vibronic coupling matrix element $\langle 2\ ^1A_g | \mathscr{H} | 1\ ^1B_u \rangle$ does not change dramatically with polyene length, an assumption supported by the results on 1,4-diphenyl butadiene and 1,6-diphenyl hexatriene, because of the larger energy gap we expect a smaller 2 ^1A_g–1 ^1B_u vibronic coupling in octatetraene than in hexatriene. The inability to detect resonance enhancement in *trans*-hexatriene therefore makes it inconceivable that the spectrum in Fig. 1 should be assigned to *trans,trans*-octatetraene.

The overall appearance of the 1 $^1A_g \rightarrow 2\ ^1A_g$ fluorescence excitation spectra of *cis,trans*- and *trans,trans*-octatetraene in low temperature *n*-alkanes are, except for intensity, superficially similar.[5,9] However, closer inspection reveals significant differences in vibronic activity. Most striking in this respect is the appearance of a mode at 1508 cm^{-1} in the spectrum of the *cis,trans* isomer which has about the same intensity as the symmetric C—C stretch vibration. An analog of the 1508 cm^{-1} mode is absent in the fluorescence excitation spectrum of *trans,trans* octatetraene in *n*-octane and appears only very weakly in the excitation spectrum of *trans,trans*-octatetraene in *n*-hexane. The 1500 cm^{-1} region of the excitation spectrum in Fig. 1 displays activity similar to that seen for *cis,trans*-octatetraene in *n*-hexane. In particular, there is a band at 1516 cm^{-1} that, on the basis of the vibronic analysis below, can only be assigned as a fundamental. This is the analog of the 1508 cm^{-1} mode that is diagnostic for *cis,trans*-octatetraene in the solid state.

In addition to the GC/MS analysis of our sample, ample evidence for the presence of the *cis,trans* isomer is also found in the 1 $^1A_g \rightarrow 1\ ^1B_u$ excitation spectrum shown in Fig. 4. The most intense peak in this spectrum is found at 35 559 cm^{-1}, in good agreement with the 0–0 transition to the 1 ^1B_u state of *trans,trans*-octatetraene as determined previously by fluorescence excitation studies[25] and absorption spectroscopy[26] on *trans,trans*-octatetratene seeded into rare gas expansions. Other vibronic bands higher in energy also agree well with the previous results. The only exception is found in the band at 35 484 cm^{-1}, 73 cm^{-1} to the red of the 0–0 transition. Leopold *et al.*[26] observed a similar band, though much weaker in intensity. They assigned this peak to a cluster peak on the basis of the dependence of its intensity on the argon stagnation pressure. Since we monitor mass selectively only the molecular ion peak of octatetraene, use helium instead of argon, and do not see any dependence of the intensity of this peak on stagnation pressure, we conclude that in our case this peak does not arise from a cluster but should rather be assigned to the 0–0 transition of the 1 ^1B_u state of *cis,trans*-octatetraene. The observed intensity of this peak relative to the *trans,trans* 0–0 transition agrees well with the *cis,trans* to *trans,trans* ratio determined in the GC/MS analysis.

Finally we consider how the conclusion that our spectra belong to the *cis,trans* isomer fit with recent results obtained on decatetraene (1,8-dimethyl-octatetraene) seeded into a supersonic expansion.[23,24] The fluorescence excitation spectrum measured for this molecule was interpreted as arising from the 1 $^1A_g \rightarrow 2\ ^1A_g$ transition of the *trans,trans* isomer with the 0–0 transition located at ~29 015 cm^{-1}. Since we know that the dipole strength of the 1 $^1A_g \rightarrow 2\ ^1A_g$ transition in hexatriene and heptatriene increases by roughly two orders of magnitude with the introduction of a double bond *cis* linkage, isomeric purity in the reservoir would have to be better than 90% to avoid seeing a *cis* isomer. Further, the assignment of the decatetraene fluorescence excitation spectrum to the *trans,trans* isomer leaves us with the problem of understanding how it is that methyl substitution can induce observable dipole strength into the 1 $^1A_g \rightarrow 2\ ^1A_g$ transition in *trans,trans*-octatetraene but not in the case of *trans*-hexatriene. It seems to us possible that the carrier of the decatetraene spectrum contains a *cis* double bond linkage.

In summary, all available data coherently support the assignment of the spectrum in Fig. 1 to *cis,trans*-octatetraene.

B. Vibronic analysis

1. Overall vibronic development

The vibronic structure in the $1\,^1A_g \rightarrow 2\,^1A_g$ excitation spectrum of *cis,trans*-octatetraene shown in Fig. 1 is in many respects what would be expected on the basis of previous solid state experiments. Most of the intensity is in four bands: the 0–0 transition and three modes with frequencies of 336, 1226, and 1799 cm^{-1}.

The 0–0 band at 29 035 cm^{-1} is 391 cm^{-1} higher in energy than in *n*-hexane and 662 cm^{-1} higher in energy than in *n*-octane. These shifts are small compared to the 3350 cm^{-1} increase in $1\,^1B_u$ excitation energy on going from an *n*-alkane crystal to the vacuum, consistent with the fact that the $1\,^1A_g \rightarrow 2\,^1A_g$ transition dipole is much smaller than the $1\,^1A_g \rightarrow 1\,^1B_u$ transition dipole.

The modes at 336, 1226, and 1799 cm^{-1} are easily identified as, respectively, a symmetric in plane bending mode (393 cm^{-1} for *cis,trans*-octatetraene in *n*-hexane, 340 cm^{-1} for *trans,trans*-octatetraene in *n*-octane), a symmetric C—C stretching mode (1228 cm^{-1} for *cis,trans*-octatetraene, 1220 cm^{-1} for *trans,trans*-octatetraene), and a symmetric C=C stretching mode (1722 cm^{-1} for *cis,trans*-octatetraene, 1754 cm^{-1} for *trans,trans*-octatetraene).[5,9] Though the activities and frequencies of these modes is in qualitative agreement with the results of the solid state experiments, there are quantitative differences.

The frequency of the mode at 336 cm^{-1} is 57 cm^{-1} lower and the relative intensity is higher than in the solid state. This is unusual since it is generally the case that vibrational frequencies are rather insensitive to environmental perturbations. The ground state frequency of this mode is 349 cm^{-1} in *n*-hexane and 346 cm^{-1} in *n*-octane,[9] values ~13 cm^{-1} higher than the gas phase 2 ^1A_g state frequency. This suggests that it is not the gas phase frequency which is anomalous. A 13 cm^{-1} drop in frequency upon excitation is in accordance with the idea that vibrational frequencies are reduced in excited states because of the more loosely bound nature of the molecule. Thus, there are grounds for believing that small external perturbations in the form of crystal fields can significantly change the properties of the 2 ^1A_g state. This idea is reinforced by an examination of the behavior of the C=C stretching mode.

As mentioned above, frequencies of the C—C and C=C stretching modes in the 2 ^1A_g state in the solid state experiments were 1228 and 1722 cm^{-1}. In the same experiments the frequencies of these modes in the ground state were 1189 and 1614 cm^{-1}. In the 2 ^1A_g state of isolated *cis,trans*-octatetraene these two modes have frequencies of 1226 and 1799 cm^{-1}. The frequency increase of these two modes upon excitation into the 2 ^1A_g state is found in all polyenes studied so far and has been explained as arising from vibronic coupling between the $1\,^1A_g \rightarrow 2\,^1A_g$ states,[12] or, formulated differently, the strong coupling of C—C stretch with C=C stretch vibrations in the 2 ^1A_g state.[27]

In *cis,trans*-octatetraene the frequency of the C=C stretching mode increases by 77 cm^{-1} in going from the solid state to the gas phase while the frequency of the C—C stretching mode remains the same. Another general (if counterintuitive) property of the 2 ^1A_g C=C stretch frequency in the solid state experiments is that it increases with increasing chain length. This is also observed in the gas phase: in the 2 ^1A_g state the C=C stretch frequency is 1724 cm^{-1} in *cis*-hexatriene and 1799 cm^{-1} in *cis,trans*-octatetraene. If we look at the changes in frequency upon excitation, the C=C mode again stands out. In *cis*-hexatriene the C—C stretch vibration has a frequency of 1123 cm^{-1} in the 2 ^1A_g state, 39 cm^{-1} higher than in the ground state, while the C=C stretch vibration has a frequency of 1724 cm^{-1}, 102 cm^{-1} higher than in the ground state.[13,14] If we assume that the ground state frequencies of the C—C and C=C stretch vibrations of *cis, trans*-octatetraene in the gas phase are about the same as in the solid state, we see that in *cis,trans*-octatetraene the C—C stretch vibration increases by 39 cm^{-1} upon excitation into the 2 ^1A_g state while the C=C stretch vibration increases by 185 cm^{-1}. Thus, on excitation to the 2 ^1A_g state the C—C stretch vibration increases by the same amount in *cis*-hexatriene and *cis,trans*-octatetraene but the frequency of the C=C stretch vibration increases 83 cm^{-1} upon the addition of one double bond. Thus, the C=C stretch vibration is peculiar in two respects: there is a large change in frequency in going from solid state to gas phase and the frequency of this mode in the 2 ^1A_g state increases with polyene chain length.

While the increase in the 2 ^1A_g C=C stretch frequency with polyene chain length may partly be ascribed to the lowering of the $1\,^1A_g \rightarrow 2\,^1A_g$ energy gap (decreasing the energy denominator in the perturbation calculation), this does not work for the frequency increase seen in *cis,trans*-octatetraene on going from an *n*-alkane matrix to the gas phase since, in this case, the $1\,^1A_g \rightarrow 2\,^1A_g$ gap increases.

While *ab initio* theory cannot address the dependence of C=C stretch frequency on environment, it can make predictions about chain length dependence. QCFF/PI *ab initio* calculation of the C=C stretch frequencies for the $1\,^1A_g \rightarrow 2\,^1A_g$ states of *trans*-hexatriene and *trans,trans*-octatetraene[12,28] predict a frequency decrease of 1 cm^{-1} (13 cm^{-1} from experiment) for the 1 ^1A_g state and an increase of 13 cm^{-1} for the 2 ^1A_g state (75 cm^{-1} from experiment) in going from hexatriene to octatetraene. The *ab initio* calculations by Aoyagi *et al.*[27] appear to do better. Although the calculated frequencies are ~20% higher than the experimental ones, they predict a decrease of 13 cm^{-1} for the 1 ^1A_g state and an increase of 51 cm^{-1} for the 2 ^1A_g state.

A rationalization of the behavior of the frequency of the C=C stretch vibration in the 2 ^1A_g state might be sought in one or a combination of the following: (i) crystal field effects; (ii) isomer geometry; and (iii) the vibronic coupling matrix element between the 1 ^1A_g and 2 ^1A_g states. Since the frequency of the C═C stretch vibration in the 2 ^1A_g state is so dramatically dependent on whether we measure in the gas phase or in the solid state (also true of the 336 cm^{-1} mode) we conclude that crystal field effects play a major role. It could be that the extent to which this influence manifests itself depends on the geometry of the molecule, that is *cis,trans*-octatetraene could be more susceptible to crystal field effects than *trans,trans*-octatetraene. From the comparison of the gas phase frequency changes upon excitation in *cis*-hexatriene and *cis,trans*-octatetraene it appears that the vibronic coupling matrix element between the 1 $^1A_g \rightarrow 2\ ^1A_g$ states changes more than *ab initio* calculations would lead one to believe. Once again, this could find its origin in the geometry of the molecule. Our experiments on various isomers of heptatriene support such a hypothesis: for 2*Z*,4*Z*-2,4,6-heptatriene a frequency of the C═C stretch vibration of 1709 cm^{-1} has been measured, for 2*E*,4*Z*-2,4,6-heptatriene 1720 cm^{-1} and for *Z*-1,3,5-hexatriene 1760 cm^{-1}.[14,15] These numbers show an unusually large dependence of the frequency on the molecular geometry. An evaluation of the importance each of the above mentioned factors awaits the results of more solid state and gas phase experiments and high quality *ab initio* calculations on the isomer dependence of the electronic structure of the linear polyene 2 ^1A_g state.

2. Analysis of weaker vibronic bands

In addition to the fundamentals, overtones and combinations of the three major modes at 336, 1226, and 1799 cm^{-1} the excitation spectrum in Fig. 1 has a rich vibronic structure of bands that have intensities between 5% and 30% of the intensity of the 0–0 transition. In the solid state the vibronic activity of the 1 $^1A_g \rightarrow 2\ ^1A_g$ transition of the *cis,trans* isomer is much higher than for the *trans,trans* isomer[9] due to the lowering of the molecular symmetry from C_{2h} to C_s in *cis,trans*-octatetraene. A complete assignment of the observed structure is not feasible and we stress that the assignments in Table I are certainly not unique. Nevertheless, some conclusions can be drawn.

We first turn our attention to the very low frequency region of the excitation spectrum. Here 33 cm^{-1} and, especially, 49 cm^{-1} bands are prominent. To establish that these bands are not hot bands (*a priori* doubtful since their widths are the same as that of the 0–0 transition) or bands deriving from single bond conformers of *cis,trans*-octatetraene we measured their intensity relative to the 0–0 transition as a function of the distance between the nozzle and the skimmer. Similar experiments on bithiophene have demonstrated that in this way we are able to dramatically change the translational, rotational, and vibrational temperatures in the jet and unambiguously establish the identity of a band.[29] Since the relative intensities of both bands were independent of the nozzle to skimmer distance, we conclude that the 33 and 49 cm^{-1} band belong to fundamentals. That at least the 49 cm^{-1} band belongs to the same molecule as the rest of the major bands is supported by presence of the combination bands with 336, 1226, and 1799 cm^{-1}.

The presence of two modes at such low frequencies raises the question of assignment. While it is true that in the solid state experiments on *cis,trans*-octatetraene the phonon sidebands of the excitation lines showed a prominent progression in a 32 cm^{-1} mode, it seems unlikely that this could be a purely intramolecular vibration. The lowest frequency observed in the excitation spectrum as a discrete band was 175 cm^{-1}.[9] The combination of one and two-phonon spectroscopy on *trans,trans*-octatetraene identified a 93 cm^{-1} b_u symmetry promoting mode. One could tentatively speculate that the 49 cm^{-1} mode in *cis,trans*-octatetraene corresponds to the 93 cm^{-1} mode in *trans,trans*-octatetraene. This would lead then to the assignment of the 33 cm^{-1} mode as the analog of the a_u symmetry mode in *trans,trans*-octatetraene calculated at 60 cm^{-1} in the ground state.[30]

The one-photon excitation spectrum of the 2 ^1A_g state of *trans,trans*-octatetraene is built on b_u symmetry vibrations with frequencies of 93, 463, 538, and 1054 cm^{-1}.[5] Given the tentative conclusion that the 49 cm^{-1} mode in the excitation spectrum of *cis,trans*-octatetraene corresponds to the 93 cm^{-1} mode in *trans,trans*-octatetraene, it is reasonable to wonder if the other promoting modes show up in the excitation spectrum of *cis,trans*-octatetraene. Inspection of Fig. 1 and Table I reveals modes with reasonable intensity, though smaller than the intensity of the 49 cm^{-1} mode, at 448, 538, and 1080 cm^{-1}. Assignment of these bands as fundamentals is buttressed by the abundant presence of combination bands with the prominent modes (see Table I). Thus, it is likely that the modes at 448, 538, and 1080 cm^{-1} correspond to the b_u symmetry promoting modes in *trans,trans*-octatetraene.

Vibrational activity in the 1100–1300 cm^{-1} region consists of only two somewhat weak bands: one at 1226 cm^{-1} assigned to the symmetric C—C stretch vibration and a band at 1275 cm^{-1} assigned to the combination band of the 1226 and 49 cm^{-1} modes. In the solid state experiments on *cis,trans*-octatetraene three bands at 1128, 1226, and 1320 cm^{-1} with an intensity ratio of ~5:4:1 were observed. The absence of the bands around 1128 and 1320 cm^{-1} in the gas phase once again indicates that the electronic structure of the 2 ^1A_g state of octatetraene is quite susceptible to small perturbations.

Finally, we come to the 1500–1600 cm^{-1} region. While a number of these bands are likely to be combination bands as indicated in Table I, the bands at 1509 and 1516 cm^{-1} must be fundamentals on the basis of both frequency and intensity. The solid state experiments showed similar activity at 1508 cm^{-1}, presumably involving the same modes.

C. Lifetimes

In Table II and Fig. 2 we give the lifetimes measured for 16 bands in the excitation spectrum of *cis,trans*-octatetraene. At the 0–0 transition we observe a lifetime of 273 ns, which is most probably determined by nonradiative processes as concluded from our study of *trans,trans*-octatetraene in various alkane matrices at 4.2 K.[18]

Up to ~1200 cm^{-1} above the 0–0 transition the measured lifetimes fluctuate around a common value. Above 1200 cm^{-1} the lifetimes decrease rapidly to the point that above 2300 cm^{-1} the decay time is so short relative to the width of the excimer laser that it cannot be measured. The fact that the bandwidths of the high lying vibronic levels are significantly broadened is an indication of the tremendous increase in the decay rate with vibronic energy above 1200 cm^{-1}. For example, the overtone of the C=C stretch vibration 3583 cm^{-1} above the 0–0 has a width of $\sim 8 \pm 2$ cm^{-1}. This implies a lifetime of the order of ps which is almost five orders of magnitude shorter than the lifetime measured at the 0–0 transition.

Vibronic coupling between the 2 ^1A_g and 1 ^1B_u states is expected to increase as the vibronic energy increases, enhancing radiative decay. However, the dependence on vibrational energy is expected to be rather smooth as in the case of isolated diphenylhexatriene where the decay rates change only by a factor of 2 over an 8000 cm^{-1} range. It is clear that precipitous decrease in lifetime between 1200 and 2300 cm^{-1} measured for *cis,trans*-octatetraene is incompatible with the idea that the decrease is due to increased vibronic coupling between the 2 ^1A_g and 1 ^1B_u states. This conclusion is also supported by the fact that above 2300 cm^{-1} no vibrational structure is observed except for the overtone of the C=C stretch vibration. If vibronic coupling were important we would have expected to see an increase in the intensity of vibronic bands.

The lifetimes measured for *cis,trans*-octatetraene most closely resembles the dependence of lifetime on vibrational energy measured for the 2 ^1A_g state of isolated diphenylbutadiene[19,31] and the lowest excited singlet state of stilbene.[32] In these molecules the decrease in lifetime has been attributed to the opening of a nonradiative decay channel involving double bond *cis-trans* isomerization. However, the association of the major break in the lifetime vs vibronic energy curve with an isomerization barrier is not as straightforward as might be hoped. Consider the supersonic jet experiments on diphenylbutadiene. As the lifetimes show a sharp decrease at ~ 1050 cm^{-1} above the 0–0 (Refs. 19 and 31) one would intuitively assume that the isomerization barrier is near this value. However, one[19] and two-photon[33] spectroscopy demonstrates that, whereas at low vibronic energy the lifetimes of *g* and *u* symmetry vibrational levels differ by a factor of 2, 300 cm^{-1} above the apparent origin they become dynamically indistinguishable. This indicates that the nonradiative decay channel responsible for the decrease in lifetime may be associated with a process other than (or, in addition to) isomerization.

Experiments on isomers of octatetraene in the solid state have shown that the barrier for the isomerization from *cis,trans*-octatetraene to *trans,trans*-octatetraene is ~ 400 cm^{-1} and that the barrier in the other direction is ~ 900 cm^{-1}.[11] The lifetime vs vibronic energy data measured for *cis,trans*-octatetraene are well fit by the simple energy threshold expression $1/\tau = 1/\tau_0 + \nu_A e^{-\Delta E/kT}$, where $\tau_0 = 267$ ns, $\nu_A = 13.5 \times 10^3$ s^{-1} and $\Delta E/hC = 307$ cm^{-1}. Given the uncertainties in the extracted barriers and the fact that intermolecular interactions are expected to raise the effective barrier in the condensed phase, the best fit threshold value of 307 cm^{-1} is suspiciously consistent with the 400 cm^{-1} barrier measured in the solid state. This suggests that *cis-trans* isomerization on the 2 ^1A_g potential energy surface is an important part of the nonradiative process that increases the decay rate at high vibronic energies.

D. Comparison with *cis*-hexatriene

We now compare the present results on *cis,trans*-octatetraene with those obtained for *cis*-hexatriene[14] in order to gain insight into the changes in the electronic structure of the 2 ^1A_g state that occur as the number of double bonds in the polyene chain is increased. In *cis*-hexatriene the doubled origin band and multiplet structure in the vibronic bands lead us to the conclusion that the molecule is slightly nonplanar in the 2 ^1A_g state, the nonplanarity being mainly localized on the terminal carbon atoms.[14] These features are missing from the spectrum of *cis,trans*-octatetraene in agreement with the conclusion that octatetraene remains planar upon excitation into the 2 ^1A_g state.[27]

The next point concerns the activities of the 336 and 1226 cm^{-1} modes in *cis,trans*-octatetraene. Analogous modes are observed in *cis*-hexatriene as a multiplet at 360 cm^{-1} and a single band at 1123 cm^{-1}.[14] Both modes are much more intense (about a factor of 6) in *cis,trans*-octatetraene than they are *cis*-hexatriene. This indicates that significantly different geometry changes occur upon excitation into the 2 ^1A_g state of *cis*-hexatriene and *cis,trans*-octatetraene, though the exact nature of these differences is not yet clear.

At energies 2000 cm^{-1} above the 0–0 and higher, in striking contrast to the situation for *cis*-hexatriene, there is almost no vibronic activity in the excitation spectrum of *cis, trans*-octatetraene. This has been rationalized as resulting from the rapid increase in the nonradiative decay rates of these levels.

Finally we consider the C=C stretch vibration and its overtone. In *cis,trans*-octatetraene the fundamental is intense relative to the 0–0 with a linewidth narrower than our laser while the overtone is extremely weak and broad. In *cis*-hexatriene the fundamental and the overtone of the C=C stretch vibration have about the same intensity and the overtone exhibits only a slight broadening. This tells us that the nonradiative channel responsible for the lifetime decrease in *cis,trans*-octatetraene, presumably in some way associated with *cis-trans* isomerization, is of far larger importance in *cis,trans*-octatetraene than in *cis*-hexatriene.

Additionally, while the *cis*-hexatriene excitation spectrum had background intensity that steadily increased with increasing vibronic energy, this background is completely absent in the *cis,trans*-octatetraene excitation spectrum. Though matters are complicated by the nonradiative channel, this suggests that the vibronic coupling matrix element between the 2 ^1A_g and 1 ^1B_u states is smaller in *cis,trans*-octatetraene than in *cis*-hexatriene.

The overall picture that emerges from these considerations of vibrational activity, nonradiative decay channels, and vibronic coupling is that the electronic characteristics of the 2 ^1A_g state of at least the shorter polyenes changes significantly as the chain is extended.

V. CONCLUSIONS

The application of two-color resonance enhanced two-photon ionization spectroscopy has enabled us to study in great detail the 1 $^1A_g \rightarrow 2\ ^1A_g$ excitation spectrum of octatetraene under isolated conditions. The vibrational structure in this spectrum and the comparison with our previous experiments on hexatriene and solid state experiments on various isomers of octatetraene establish that this spectrum derives from *cis,trans*-octatetraene and not from *trans,trans* octatetraene, the isomer that is the majority species in our samples. Though qualitatively the excitation spectrum agrees well with the general conclusions that have been drawn from solid state experiments on the nature of the polyene 2 ^1A_g state, a quantitative comparison of intensities and frequencies of the vibronic structure reveals that this electronic structure is susceptible to small crystal field perturbations.

The lifetime of the zero point level of the 2 ^1A_g state is 273 ns. As the vibrational energy increases the lifetime decreases sharply at ~ 1200 cm^{-1}, dropping by an order of magnitude over an energy range of ~ 1000 cm^{-1}. This fast decrease should, at least in part, be attributed to *cis-trans* isomerization processes, though the 1200 cm^{-1} edge is not necessarily simply related to the isomerization barrier.

Comparison of these results with our previous results on hexatriene indicates that the observation of the one-photon 1 $^1A_g \rightarrow 2\ ^1A_g$, excitation spectrum of the *all-trans* isomers of linear polyenes under isolated conditions will be very difficult unless the electronic structure of the polyene chain is significantly altered. This comparison also showed that the electronic structure of the polyene changes considerably upon going from three to four conjugated double bonds.

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