explanation in both cases. A similar change in $\Delta E°$ (anti–gauche) upon going from the vapor phase to solution is to be expected for other hydrazines, and should be employed if PE estimates of conformational mixtures are to be used in the rationalization of experiments conducted in solution.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie (Marburg) as well as the National Science Foundation (Wisconsin). The calculations were carried out by using the TR 440 computer at the Rechenzentrum der Universität Marburg.

Time-Resolved Resonance Raman Spectroscopy: The Excited Triplet State of *all-trans*-β-Carotene

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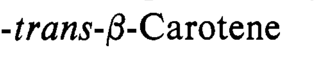
Abstract: The lowest excited triplet state of *all-trans*-β-carotene produced by pulse radiolysis has been studied by time-resolved resonance Raman spectroscopy. Six transient Raman bands at 965, 1009, 1125, 1188, 1236, and 1496 cm^{-1} were observed. The assignment of these transient bands to the triplet state of β-carotene is based on measurements of the dependence of the intensity upon irradiation dose and time. The Raman intensity was found to have the same dose and time dependence as the transient optical absorbance. The spectrum is discussed in detail, and it is concluded that the C=C double bond order is decreased in the triplet state and that the molecule may be substantially twisted, presumably at the 15,15′ bond, in the triplet state. The downward shift of the strong band in the C–C stretching region to 1125 cm^{-1}, however, still remains unexplained.

Introduction

The study of excited states of conjugated polyenes such as carotenes is of considerable interest in the understanding of photosynthesis. Previous studies of the lowest excited triplet state of *all-trans*-β-carotene in vitro include flash photolysis[1,2] and pulse radiolysis[3–5] experiments. All of these are based on the observation of a very strong transient optical absorption in the 510–530-nm region, which is due to the lowest triplet–triplet transition in β-carotene.

β-Carotene and related polyenes are also known to exhibit extremely strong enhancement in resonance Raman scattering. A large number of workers[6–15] have reported on different aspects of the resonance Raman spectrum of the ground state of β-carotene.

A few years ago, the technique of resonance Raman spectroscopy was extended by us to the study of short-lived radicals[16,17] and excited triplet states;[18] other groups[19–23] have reported on similar work. Recently Woodruff and co-workers[24] published the first time-resolved resonance Raman spectrum of the lowest triplet state of *all-trans*-β-carotene using pulse radiolysis. These authors detected three vibrational bands at 1495, 1126, and 1014 cm^{-1}, which were correlated to the ground-state in-phase double bond C=C stretching mode at 1521 cm^{-1}, the C—C in-plane single bond stretching mode at 1157 cm^{-1}, and a C—H in-plane bending mode at 1005 cm^{-1}, with the respective shifts when going to the triplet state. We report here a study under similar conditions essentially confirming the results of Woodruff and co-workers, but additionally finding three vibrational bands of the transient excited state at 965, 1188, and 1236 cm^{-1} and giving details with respect to the dependence of the vibrational spectra on time and the delivered irradiation dose.



ALL-trans β-CAROTENE

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Experimental Section

all-trans-β-Carotene was supplied from Sigma and used without further purification. Naphthalene (scintillation grade) was obtained from Merck. Benzene (Merck p.a.) was passed through a column packed with neutral alumina (Woelm) before use. Solutions of β-carotene in benzene (10^{-4} M) containing 10^{-2} M of naphthalene as sensitizer in order to populate the polyene triplet state efficiently were flushed for 0.5 h with Ar before using. The electron irradiation facilities and the electrooptical multichannel spectrometer for the detection of Raman scattered light are described in detail elsewhere.[25] Only the essential features shall be given here. Solutions were irradiated with a pulse of 2-MeV electrons of 30-ns duration, and changes in optical absorption were detected in the usual way by analyzing the light from a Xe lamp transmitted through the reaction cell. Resonance Raman spectra were excited by a pulse of 600-ns duration from a tunable dye laser with variable time delay with respect to the electron pulse. The transient resonance Raman spectra of triplet β-carotene reported below were all excited at 531.1 nm. The scattered light was detected by means of an optical multichannel spectrometer gated for 1 μs in order to discriminate against Cerenkov light. The data were processed by a computer. The spectral resolution of the system was limited by the laser bandwidth to 20 cm^{-1} in order to obtain sufficient laser pulse energy. The main differences compared to the work of Dallinger et al. are (1) the higher irradiation dose of ~68 krad in our experiments which allowed the generation of excited states at correspondingly higher concentrations, (2) the longer laser pulse duration, and (3) the fact that our spectra are recorded with single pulses, changing the solution after each pulse.

Results and Discussion

The spectral and kinetic characteristics of the chemical system 10^{-4} M β-carotene in benzene containing 10^{-2} M naphthalene were investigated in detail by optical absorption spectroscopy. These measurements, which will be reported elsewhere,[26] gave several results of importance for the present study.

The absorption spectrum obtained with an irradiation dose of 1.7 krad had λ_{max} = 530 nm, which compares well with the results of Mathis and Kleo[2] obtained by chlorophyll *a* sensitized flash photolysis of β-carotene in benzene. However, this value differs from the value of 515 nm reported by Dallinger et al.[24] Presumably they used the value obtained by Land et al.[3] with *n*-hexane as solvent.

In estimating the radiation chemical yield of triplet β-carotene, we first calibrated the relative doses by measuring the optical densities of triplet naphthalene obtained by irradiation of 10^{-2} M naphthalene in benzene. By using $G\Delta\epsilon_{max} = 3.58 \times 10^2$ eV^{-1} M^{-1} cm^{-1} [27] for triplet naphthalene the effective doses could be calculated. From our measurements on β-carotene, we obtained $G\Delta\epsilon_{530} = (2.75 \pm 0.25) \times 10^3$ eV^{-1} M^{-1} cm^{-1} for the production of triplet β-carotene in benzene containing 10^{-2} M naphthalene and 10^{-4} M β-carotene. Using $\Delta\epsilon_{max} = 2.38 \times 10^5$ M^{-1} cm^{-1},[4] we get $G = 1.15 \times 10^{-2}$ eV^{-1} for the effective yield of triplet β-carotene. As $\Delta\epsilon_{max} = 1.32 \times 10^4$ M^{-1} cm^{-1} for triplet naphthalene in benzene,[28] this *G* value indicates that ~42% of the triplet naphthalene molecules were quenched by β-carotene.

The *G* value for formation of triplet β-carotene was constant up to a dose of at least 25 krad as plots of maximum absorbance vs. dose were linear.[26] The *G* value probably decreases at higher irradiation doses, but we estimate that approximately 50% of the β-carotene molecules were excited to the triplet state at the maximum dose used for resonance Raman experiments.

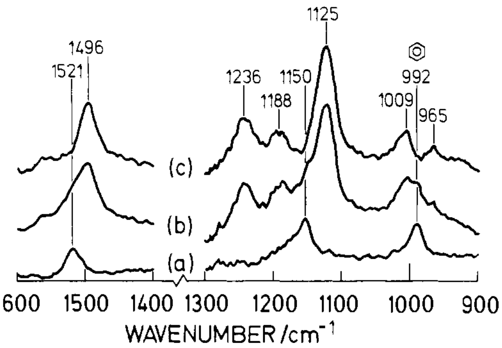

Figure 1. Resonance Raman spectra from 10^{-4} M *all-trans-β*-carotene in benzene containing 10^{-2} M naphthalene. (a) Background spectrum without electron irradiation. (b) Spectrum recorded 1 μs after electron irradiation. (c) Difference spectrum (b − a). Irradiation dose = 68 krad, laser excitation wavelength = 531.1 nm, spectral segments recorded with single pulses. Unsmoothed spectra.

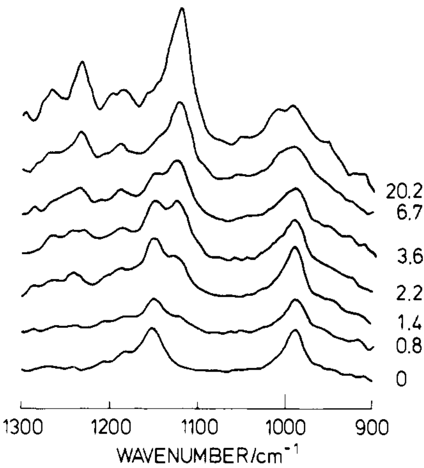

Figure 2. Resonance Raman spectra recorded after electron irradiation of 10^{-4} M *all-trans-β*-carotene in benzene containing 10^{-2} M naphthalene with the relative doses indicated. Laser excitation wavelength = 531.1 nm. All spectra were recorded 1.7 μs after the electron pulse except the spectrum at the highest dose, which was recorded 1 μs after the electron pulse. Smoothed spectra.

Table I. Vibrational Frequencies (cm^{-1})

ground state				triplet excited state	
Rimai et al.[a]	this work	Dallinger et al.[b]	this work	Dallinger et al.[b]	this work
CW-excit	CW-excit	pulsed	pulsed	pulsed	pulsed
n-hexane	benzene	benzene	benzene	benzene	benzene
488 nm	514.5 nm	531.8 nm	531.1 nm	531.8 nm	531.1 nm
961 vw					965 ± 13 w
1006 w	1005 w	1003		1014	1009 ± 3 m
1158 vs	1157 vs	1157	1150	1126	1125 ± 2 vs
1193 w	1190 w				1188 ± 3 m
1215 vw	1213 vw				1236 ± 3 s
1527 vs	1520 vs	1521	1521	1495	1496 ± 2 vs

[a] Reference 7. [b] Reference 24.

Figure 1b shows the resonance Raman spectrum obtained with an irradiation dose of ~68 krad. The delay of the laser pulse with respect to the electron pulse was adjusted so that the sample was probed at a time when the triplet concentration was near its maximum. Figure 1a shows the background spectrum without electron irradiation and Figure 1c is the difference spectrum (1b − 1a) showing the bands of the transient only. The vibrational frequencies are tabulated in Table I along with data on ground state β-carotene and the results of Dallinger et al.[24] Before proceeding with a discussion of these experimental observations, we present evidence for the assignment of the transient resonance Raman bands to the excited triplet state of β-carotene.

Figure 2 shows a series of resonance Raman spectra obtained at various irradiation doses. The doses varied between 2.8 and 68 krad. For comparison a background spectrum without irradiation, but under otherwise identical conditions, is shown in the lower trace. It can be seen that the intensity of the transient Raman bands increases with increasing dose. Figure 3 shows the relative Raman intensity at 1125 cm^{-1} as a function of the relative irradiation dose. The points were obtained by measuring the

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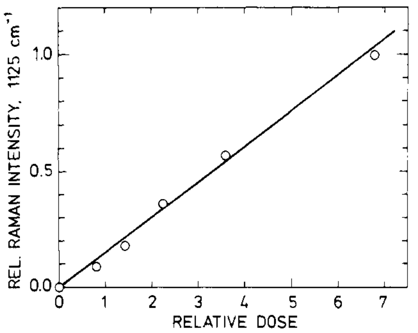

Figure 3. Raman intensity at 1125 cm^{-1} vs. relative irradiation dose. See text for discussion.

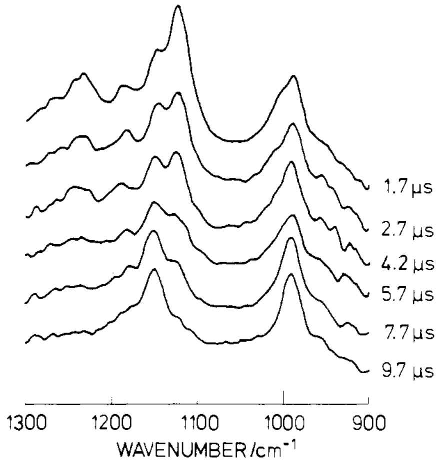

Figure 4. Resonance Raman spectra recorded at various delays of laser pulse with respect to electron pulse. Irradiation dose was constant = 17.6 krad, solution: 10^{-4} M *all-trans-β*-carotene in benzene containing 10^{-2} M naphthalene, laser excitation wavelength = 531.1 nm. Smoothed spectra.

1125-cm^{-1} intensity relative to the intensity of the benzene band at 992 cm^{-1} in the spectra shown in Figure 2, neglecting the difference in absorbance due to different wavenumbers.[29] Thus the transient optical absorbance[26] and the transient Raman intensity have qualitatively the same dose dependence, indicating a common origin of the two observable quantities. The transient band at 1125 cm^{-1} is still detectable at a relative dose of 0.81 (2.8 krad), corresponding to a triplet concentration of ~2.9 × 10^{-6} M.

Figure 4 shows a series of spectra obtained at various delays after the electron pulse, but at a constant relative irradiation dose of 5.29. This dose corresponds to 17.6 krad and lies within the dose range where a linear relation between Raman intensity and irradiation dose was found (Figure 3). The spectrum obtained at 1.7-μs delay corresponds to maximum transient concentration. From these spectra an effective half-life of 2.5 ± 0.5 μs is obtained. This value is in good agreement with the value 2.3 μs obtained from the transient optical absorbance measurement at identical irradiation dose as shown in Figure 5. As seen in Figure 4, all transient bands show qualitatively the same time dependence. On the basis of the dose and time dependence of the transient Raman bands, we are confident that these bands originate from the lowest excited triplet state of β-carotene. No indication of photoisomerization products from the ground state appeared.

Rimai et al.[8] have presented a vibrational analysis of the polyenes including β-carotene. Their important conclusions were

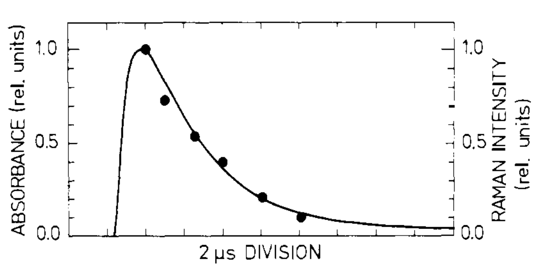

Figure 5. Optical absorbance (full line) and Raman intensity at 1125 cm^{-1} (points) vs. time. Conditions as in Figure 4.

that the bands at ~1500 cm^{-1} are adequately described as C═C stretching modes, the frequency being sensitive to the double bond character of the formal C═C bonds. The bands in the 1100–1300-cm^{-1} region contain large contributions from C—C stretching and C—C—H in-plane deformations as well as some C═C stretching. However, the bands in this region cannot be described in terms of a single type of bond. For β-carotene the band at 1005 cm^{-1} is most likely due to C–CH_3 stretching, as this band is present in all natural polyenes containing the isoprenoid elements. Finally, the band at 961 cm^{-1} can be described as in-plane angular deformation of C–C–C and C–C–H.

With these qualitative assignments in mind, we are now able to discuss the spectral features observed for the lowest excited triplet state. When correlating the triplet Raman bands with the bands of the parent ground-state molecule, frequencies as well as intensities should be taken into account. The triplet bands at 965 and 1009 cm^{-1} are most likely due to the same modes as the parent bands at 961 and 1005 cm^{-1} because of their frequencies and relative intensities. This correlation is supported by the descriptive assignments given above for the parent bands. First, the frequencies of C–C–C/C–C–H bending modes have previously been predicted to be nearly independent of partial bond order changes,[30] and recent experimental resonance Raman studies of radical ions have confirmed these predictions.[31] Second, the C–CH_3 bonds are largely unconjugated with the π electrons of the alternating double bonds in the polyene chain. Thus, neither the C–C–C/C–C–H angular deformation modes nor the C–CH_3 stretching modes are expected to be influenced by the electronic excitation.

The bands at 1125, 1188, and 1236 cm^{-1} show an intensity pattern not found in the ground state spectrum (see Table I). Only the band at 1125 cm^{-1} seems to be correlated with the ground-state band at 1157 cm^{-1}, indicating a shift of 32 cm^{-1} to lower frequency. This frequency shift will be discussed later. The bands at 1188 and 1236 cm^{-1} have intensities relative to the 1125-cm^{-1} band which do not justify direct correlation with the ground-state bands at 1190 and 1213 cm^{-1}. In particular, the transient band at 1236 cm^{-1} is much stronger compared to the bands at 1125 and 1188 cm^{-1} than the ground-state band at 1213 cm^{-1} compared to the bands at 1157 and 1190 cm^{-1}. Furthermore, it should be noticed that the high relative intensities of the 1188-/1236-cm^{-1} bands are probably not due to specific enhancement effects, as the intensity pattern of the spectra did not change by using laser excitation at longer wavelengths.[32] Thus, the transient bands in the 1100–1300-cm^{-1} region most likely reflect a conformational change of *all-trans-β*-carotene in the excited triplet state as compared with the ground state.

Lutz et al.[33] have reported on the low-temperature resonance Raman spectra of *all-trans-β*-carotene and 15,15′-*cis-β*-carotene. The most striking difference in the spectra of the two isomers is the appearance of a pair of strong bands at 1245/1237 cm^{-1} and an intensity enhancement of the bands at 1194 and 955 cm^{-1} in

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(29) Different transient Raman bands will generally be attenuated differently when the concentration of the transient species (i.e., the transient absorbance) is changed. In the present case, however, the differences in transient absorbance at different nearby wavenumbers can be neglected as the bands at 1125 and 992 cm^{-1} only span ~4 nm around 563 nm on the wavelength scale. This wavelength is at the red tail of the transient triplet-triplet absorption, where the transient absorbance is varying slowly with wavelength.[26]

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the spectra of the cis isomer. The strong band at 1160 cm^{-1} remains unshifted while the band at 1530 cm^{-1} shifts to 1540 cm^{-1} in the cis isomer. Rimai et al.[34,35] have investigated the Raman spectra of a series of isomers of retinal. They found that the most prominent changes in the spectra occurred in the 1100–1400-cm^{-1} region. In particular, the various cis isomers are characterized by specific new bands in this spectral region as compared to the all-trans isomer.

Taking these observations into account, we believe that the observed changes in the Raman spectra in going from the parent ground-state compound to the lowest excited triplet state indicate substantial C=C bond twisting in the equilibrium conformation of the triplet state. In particular, the new feature at 1236 cm^{-1} in the triplet spectrum suggests that the bond twisting of the triplet excited β-carotene is localized at the 15,15′ double bond.

The interpretation of the triplet Raman spectrum suggested here is qualitatively supported by the similarity between the triplet–triplet absorption spectra of *all-trans-β*-carotene and 15,15′-*cis-β*-carotene[4,5] and by theoretical predictions based on molecular orbital calculations.[36,37] As far as the present discussion is concerned, these calculations predicted double bond twisting of the polyenes in their excited states. Twisting of the inner double bonds was preferred energetically as compared with twisting of outer double bonds.

The remaining band at 1496 cm^{-1} in the triplet spectrum can be correlated with the ground-state band at 1520 cm^{-1}, resulting in a shift of 24 cm^{-1}. As the ground-state band at 1520 cm^{-1} is probably due to in-phase C=C stretching vibrations, the observed shift upon excitation can be explained qualitatively by the decreased π-bond order in the excited state which has been predicted.[36,37]

Lutz et al.[33] reported that the strong C=C band of *all-trans-β*-carotene at 1530 cm^{-1} in their spectra shifted to 1540 cm^{-1} in the spectrum of 15,15′-*cis-β*-carotene. Assuming that our interpretation of the triplet spectrum of *all-trans-β*-carotene given above is adequate, we may notice that two opposing effects are operating. One is the electronic effect caused by the electronic excitation and the other the conformational effect due to the change in equilibrium geometry. Thus the shift due to the electronic excitation alone should be greater than 24 cm^{-1}.

Having discussed the frequency shift of the 1520-cm^{-1} ground-state band in terms of the decreased π-bond order of the excited state, the 32-cm^{-1} downward shift of the 1157-cm^{-1} ground-state band remains to be explained. Although the 1157-cm^{-1} mode contains a minor contribution from C=C stretching according to Rimai et al.[8] the shift can hardly be explained by the theoretically predicted decrease in π-bond order upon excitation, as this decrease should be accompanied by a bond order increase in the single bond regions. Twisting of the 15,15′ bond in the excited state cannot explain the shift either, as Lutz et al.[33] reported the strong band at 1160 cm^{-1} in both isomers. On the basis of their resonance Raman spectrum of the triplet β-carotene, Dallinger et al.[24] proposed that the 1005-cm^{-1} band might be due to the C—C stretching mode, as they observed a minor upward frequency shift for this band. Our measurements do not support this assignment as the shift from 1005 to 1009 cm^{-1} is insignificant; thus they agree with the assignment of this band to the C–CH_3 stretching mode. In conclusion we must leave the question open and note, as Dallinger et al. did, that these resonance Raman data may indicate that the force constants in the C–C stretching region are not changing in the predicted manner. Studies on related structures might help in resolving this problem.

Conclusions

The resonance Raman spectrum of the lowest excited triplet state of *all-trans-β*-carotene has been obtained and the assignment of the transient bands supported by investigating the dose and time dependence of the Raman intensity. The frequency and intenisty changes observed in going from the ground-state molecule to the triplet excited molecule suggest that the *all-trans-β*-carotene in its lowest excited triplet state is twisted, presumably about the 15,15′ bond. The shift observed for the ground-state band at 1157 cm^{-1}, however, cannot be qualitatively explained in terms of the suggested geometry changes.

Acknowledgments. We are grateful to Paul-Anker Lund (University of Copenhagen) for recording in the CW-excited resonance Raman spectrum of *all-trans-β*-carotene and to Jytte Eriksen, Anne Nielsen, and Preben Genske for technical assistance.

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Intermediate Molecular Species in the Oxidation of H_2S. An ab Initio Configuration Interaction Study

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Abstract: An ab initio configuration interaction method has been applied to the study of the intermediate products H_2SO, HSO, and HSOH of the oxidation reaction of H_2S in an argon matrix. The variation of energy with respect to SH asymmetric stretch is determined near the equilibrium geometry for H_2SO, and the SH bonding energy is estimated. HSOH is found to be more stable than H_2SO. A normal coordinate analysis of the former gives a frequency assignment in good agreement with matrix IR spectroscopy.

Introduction

The reaction between atomic oxygen, $O(^3P)$, and hydrogen sulfide, H_2S, has been widely studied due to its occurrence in fuel combustion and in polluted earth atmosphere. In the earlier investigations[1–4] the temperature and pressure were varied over

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