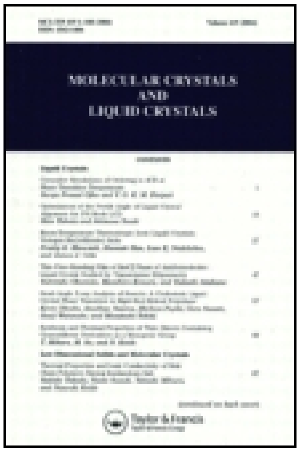

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First Detection of the (Nonphosphorescent) Triplet State in Single Crystals of β-Carotene

Jürgen Frick [a] , Jost Ulrich Von Schütz [a] , Hans Christoph Wolf [a] & Gerd Kothe [a b]
[a] 3. Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57/*55, D-7000, Stuttgart 80, Fed. Rep. of Germany
[b] Institut für Physikalische Chemie, Universität Stuttgart, Pfaffenwaldring 57/*55, D-7000, Stuttgart 80, Fed. Rep. of Germany

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FIRST DETECTION OF THE (NONPHOSPHORESCENT) TRIPLET STATE IN SINGLE CRYSTALS OF β-CAROTENE

JÜRGEN FRICK, JOST ULRICH VON SCHÜTZ, HANS CHRISTOPH WOLF,
AND GERD KOTHE*
3. Physikalisches Institut, *Institut für Physikalische
Chemie, Universität Stuttgart, Pfaffenwaldring 57/*55,
D-7000 Stuttgart 80, Fed. Rep. of Germany

Abstract Time resolved ESR on the photoexcited triplet state of β-carotene single crystals have allowed the first correlation of the fine structure tensor with the molecular axes system. Both roughly coincides within 20°. The fine structure parameters are $D = 0.0331\ cm^{-1}$ and $E = 0.0040\ cm^{-1}$.

INTRODUCTION

Triplet states in carotenoids were accessible so far only via triplet-triplet energy transfer from strongly polarized photosensitizers, as, e.g. the chlorophylls in photosynthetic reaction centers[1]. This is due to the low quantum yields for singlet-triplet intersystem crossing in competition to strong radiationless decay channels. All the system so far where randomly oriented.

Recently we succeeded to detect triplet states in crystalline β-carotene using pulsed laser excitation and time resolved ESR. The regular arrangement of the molecules[2] makes a direct correlation of the fine structure properties and the molecular axes of the "all trans" β-carotene molecules feasable.

EXPERIMENTAL

Using a diffusion zone technique[3], large single crystals of ca. $10x10x0.5\ mm^3$ were grown. The optical excitation was performed into the singlet manifold at 600 nm by a pulsed N_2- and dye-laser. Although in cw-ESR not detectable, transient nutations in a constant B_1-field with appreciable S/N-ratio were obtained after pulsed optical excitation.

RESULTS

Representative for all signals the temperature dependence of the amplitude evaluation after the laser pulse is given in Figure 1. Always two sets of triplet signals have been found (Figure 2).

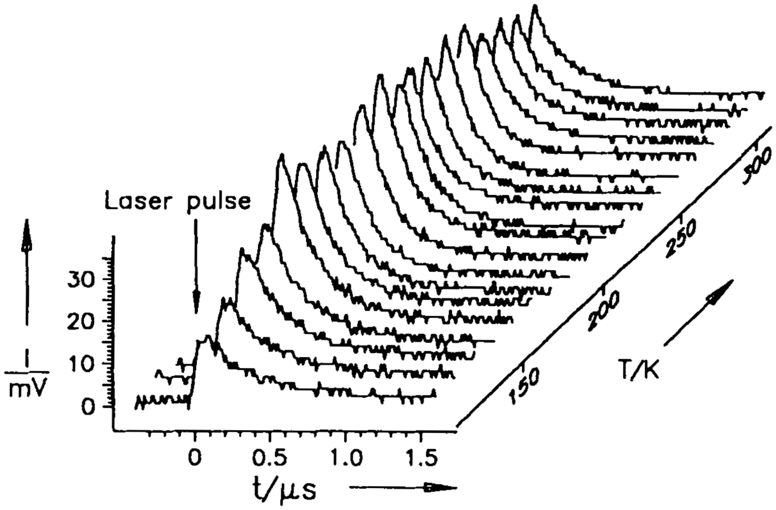

FIGURE 1 Decay of the spinpolarization in the temperature range 120 K ≤ T ≤ 300 K

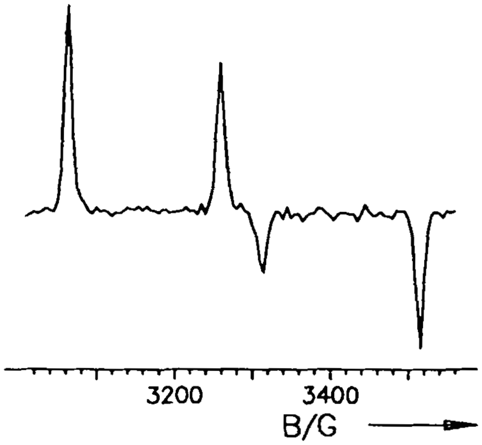

FIGURE 2 Signal amplitude at t = 0.2 μsec (see Figure 1) as function of the magnetic field.

DATA EVALUATION AND DISCUSSION

The sets of triplet signals have identical fine structure parameters of D = 0.0331 cm^{-1}, E = 0.0040 cm^{-1}. The values agree with measurements of other authors in frozen solution.[4,5] The angular dependence of the triplet resonances on rotation of the crystal coincides with the symmmetry of the two non equivalently oriented carotenes in the unit cell. The main axis of the FS-tensor is roughly in direction of the chain (see Table I).

TABLE I Angular position of the fine structure tensor

angle (molecular chain-axis, $\hat{Z}$)	= 18±10°
angle (normal in chain-plane, $\hat{X}$)	= 26±10°
angle (normal out of chain-plane, $\hat{Y}$)	= 18±10°

The small deviation from the chain direction cannot be explained in the momentary state. We do not believe in a full spin density on the rings which are thought to be decoupled partly from the main chain by the twisted arrangement of side groups. It cannot be excluded, however, that the molecules are bent in the excited state.

In Table II the D and E values of the β-carotene are confronted to further triplet data of conjugated systems, differing in the chain length. As expected, D ~ 1/n is a good measure for the delocalization of the excitation.

TABLE II Fine structure values of some polyenes

n	Name	$\|D\|/cm^{-1}$	$\|E\|/cm^{-1}$	Ref.
6	Carotenophorphyrin	0.0682	0.0068	6
9	Neurosporene	0.0365	0.0035	7
10	Sphaeroidene	0.0335	0.00349	8
11	β-Carotene	0.0331	0.0040	this work
	Rhodopin	0.0281	0.00302	9
12	Rhodovibrin	0.0260	0.00284	10
13	Spirilloxanthin	0.0231	0.00261	10

The D value of β-carotene is much closer to that of a n = 9 system than to that of rhodopin (n = 11) which has "open rings" at the end, a further indication of the statement given above. In accordance to that is also the blue shift of the β-carotene singlet absorption in respect to lycopene (n = 11 all-trans)[11].

Dynamics

In order to distinguish between localized and mobile triplet states (excitons) polarization and decay rates were evaluated. They vary between 120 and 300 K (the temperature range accessible so far) only by roughly 30%. The decay constant is in the order of 250 nsec and is therefore between 1 and 2 orders of magnitude shorter than the triplet lifetime of β-carotene in solution. The reason for this enhanced relaxation is still unclear and could be discussed in terms of spin lattice relaxation or various lifetime limitations.

The lack of any resolved Rabi oscillations at B_1-fields up to $3x10^{-5}$T (0.8 MHz) points towards a homogenous linewidth of $1/T_2 >$ $5x10^{6}$ sec^{-1}. This is comparable with the decay time and lets open the question whether the homogeneous part of the total linewidth ($2x10^{-3}$T) is lifetime (relaxation) limited, too.

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