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SOLITONS IN DOPED β-CAROTENE FILMS: OPTICAL ABSORPTION AND ESR STUDIES

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ABSTRACT

We present optical absorption and electron spin resonance studies of iodine and AsF_5 doped β-carotene films. We show that stable soliton-like defects are formed upon p-doping. The spin to charge ratio found experimentally is $\simeq$0.02, indicating that nearly all defects are spinless. The absorption spectrum is characterized by a single intragap band and a set of infrared active vibration lines; evidence that there is significant structural relaxation upon charge transfer. A possible spinless species is the dication in which two soliton defects are formed. The small number of spins observed are probably due to β-carotene radical cations.

INTRODUCTION

Trans-β-carotene is a conjugated molecule which consists of a backbone of eleven double bonds, as shown in Fig. 1a. Its backbone is similar to that of *trans*-polyacetylene with four methyl groups placed symmetrically about the molecule center. It is therefore expected that its electronic properties are similar to those of *trans*-polyacetylene of fixed length of about 22 carbon bonds. In particular, the charge storage states upon doping is of fundamental importance, since spinless charged states ("charged solitons") were found [1] in long *trans*-polyacetylene, but are not expected in very short conjugated molecules. The intermediate length of β-carotene makes it attractive to study the spin-charge relation of the charge storage state.

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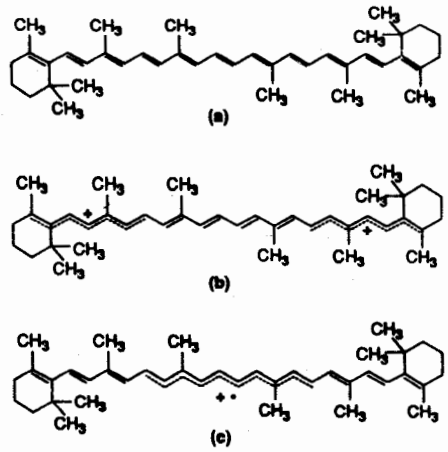


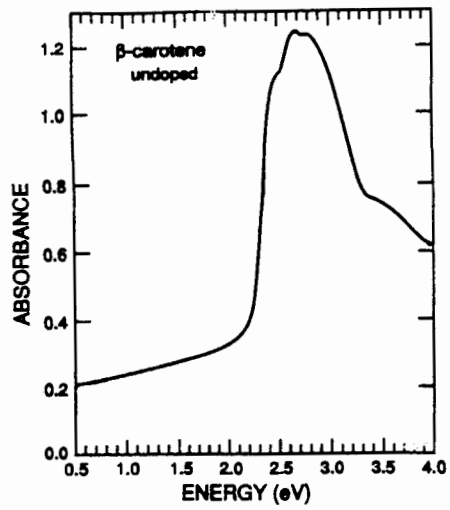


Fig. 1. (a) The chemical structure of β-carotene. Suggested structures: (b) for the dication β-C^{++}, and (c) for the radical cation β-$C^{\bullet+}$.

Fig. 2. The absorption spectrum of undoped β-carotene film at room temperature.

Recent electrochemical studies of β-carotene in solution showed an oxidation process involving the transfer of two electrons to form the dication, β-C^{++} [2]. In the presence of excess β-carotene, however, these dications are apparently unstable and decay into singly charged radical cations which subsequently decay further in a matter of minutes. An unstable doped state was also observed upon doping with iodine in solutions [3].

Here, we present the results of optical absorption (in the range 0.2 to 4.0 eV) and ESR studies of thin films of β-carotene, which are stable for a relatively long period of time. We show that upon p-doping with either iodine or AsF_5, charge is stored in a spinless, stable configuration accompanied by structural relaxation of the β-C molecule. A possible spinless species is the dication β-C^{++} in which a pair of solitons are formed within the β-carotene molecule. The formation of such dications is confirmed by calculations, and the calculated absorption spectrum is in agreement with the experimental results.

Previously, optical absorption and ESR studies of doped β-carotene were reported by various authors [4–8]. However, no quantitative estimate of the spin/charge ratio could be obtained and thus the nature of the positively charged state of p-doped β-carotene remained unresolved. In the present study, we have used in-situ doping methods for the optical absorption as well as ESR studies to obtain quantitatively the spin/charge ratio.

RESULTS

Optical absorption and ESR

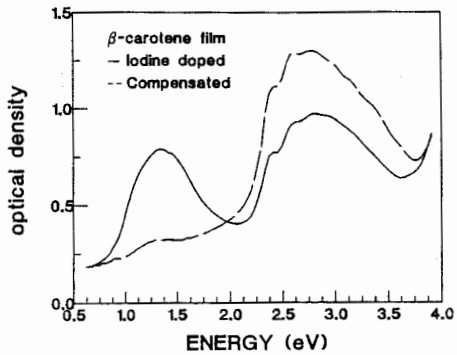
The initial β-carotene material was 99% trans in the form of a crystalline powder obtained from Kodak. Prior to use, it was kept in a freezer in the dark. Films were made by dipping a quartz glass (or KBr) substrate into a chloroform solution of β-carotene and subsequently drying it in an argon atmosphere. The resulting films were typically of optical density of 1–2 (approximate thickness $\simeq$0.1 μm) and their absorption spectrum showed resolved vibronic structure without significant scattering due to inhomogeneity (Fig. 2). Doped β-carotene samples were obtained by exposing the films to either I_2 or AsF_5 low-pressure vapor for short times.

The absorption spectrum of an undoped film of β-carotene is shown in Fig. 2, for the range 0.5 to 4 eV. The spectrum consists of the HOMO-LUMO absorption band which peaks at 2.67 eV and two shoulders at 2.48 eV and 2.85 eV due probably to vibronic structure. Compared with the absorption spectrum of β-carotene in chloroform solution, the spectrum shown in Fig. 2 is only slightly broadened, indicating a good quality film. Fig. 3 shows the results of iodine doping and de-doping experiments. First, the β-carotene film was exposed, at room temperature, for about 2 minutes to the vapor pressure of I_2, producing doped β-carotene (solid line, Fig. 3). Then, the film was exposed for 2–3 seconds to dilute aqueous solution of NH_4OH, giving rise to the spectrum shown as a broken line in Fig. 3. Comparing this spectrum to the absorption spectrum of undoped β-carotene (Fig. 2), we conclude that the doping process is reversible.

Fig. 3 shows that upon doping a new absorption band emerges at energies below the HOMO-LUMO while the HOMO-LUMO absorption band itself decreases in intensity. The doping related absorption band is peaked at 1.35 eV, and its integrated intensity is approximately equal to the decrease in the integrated intensity of the HOMO-LUMO band.

The mid-IR absorption spectrum of the doped film is shown in Fig. 4. Three strong, doping related IR absorption bands were observed at 990, 1130 and 1470 cm^{-1}. Although these lines were clearly observed, their peak absorbance is about an order of magnitude smaller than that of the 1.35 eV band. Some additional, weaker, absorption lines were found in the range 400–1500 cm^{-1}, but no other strong absorption band was observed below 4000 cm^{-1}. These infrared active vibration (IRAV) lines are additional evidence for the geometry relaxed structure of the positively charged β-carotene.

We have carried out ESR studies of the same films both before and after doping. Prior to doping there was no ESR signal observed in our films (at room temperature), and we thus estimate the concentration of spins there as less than 10^{-3} spins/molecule. Upon doping, there emerges an ESR line at g$\simeq$2.0 whose width at room temperature is $\Delta H_{pp}\simeq$10 G. We have estimated the number of spins in the doped films using a Ruby standard and calculated the ratio of spins per β-carotene molecule using the optical densities of the undoped films.



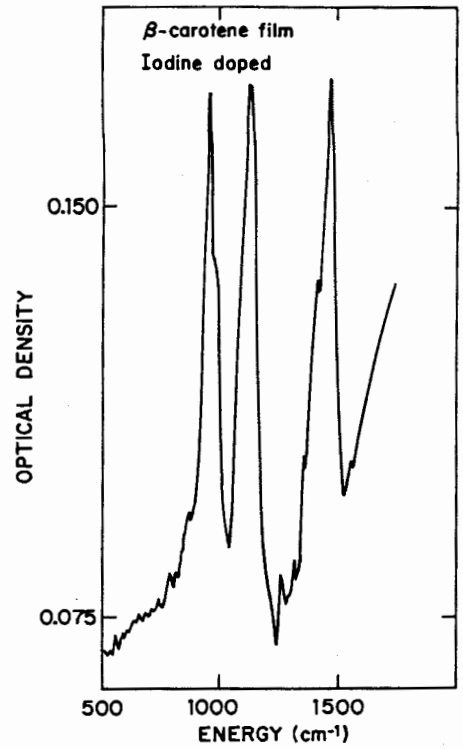


Fig. 3. The absorption spectra of iodine doped β-carotene film (solid line) and the same film after compensation with NH_4OH (broken line).
Fig. 4. Mid-IR spectrum of iodine doped film.

Estimating the doping level from the shift of oscillator strength from the HOMO-LUMO band to the doping related band, we find $\simeq 2 \times 10^{-2}$ spins per charged β-carotene molecule. Similar results were obtained for AsF_5 doping.

Calculated molecular and electronic structure

The calculations were performed using the Hartree-Fock semiempirical Austin Model 1 (AM1) technique. The detailed results were reported in a previous publication [9] and here we review mainly the results for the doubly charged β-C^{++}.

In the doubly charged molecule, strong structural relaxation is found corresponding to the formation of two bond-alternation reversals, each centered 8 sites away from the center of the molecule and each extending over $\simeq$7 carbons, as shown schematically in Fig. 1b. The presence of the two charged solitons causes the appearance of two electronic states, separated by 0.4 eV, within the HOMO-LUMO "gap" of β-carotene.

The absorption spectra were simulated utilizing Intermediate Neglect of differential Overlap / Configuration Interaction (INDO/CI) calculations including electron correlations. In the neutral case, almost all the oscillator strength is concentrated into the first electronic transition (which can be described as mostly HOMO$\rightarrow$LUMO promotion and to a lesser extent HOMO$-1\rightarrow$LUMO$+1$ promotion). As a result of the formation of the two solitons in the doubly charged compound, the first optical transition is calculated to shift down by 1.0 eV and to keep the same oscillator strength (the transition now corresponds to a combination of HOMO to lower soliton level promotion and, to a smaller degree, HOMO-1 to upper soliton level promotion).

The fact that only a single "midgap" absorption band (Fig. 3) appears despite the presence of two separated one-electron soliton levels follows directly from symmetry. The symmetries of the π-electron states of β-C and β-C^{++} are alternatively gerade (g) and ungerade (u) as a function of increasing energy. The promotion of an electron from the HOMO level (g) of β-C^{++} to the lower soliton level (u) is thus one-electron allowed (B_u transition) while that to the upper soliton level (g) is one-electron forbidden (A_g transition). The theoretical results thus fully confirm the experimental data in that the two-soliton formation upon doping leads to a single absorption in the "gap", which steals all its intensity from the original HOMO$\rightarrow$LUMO absorption band.

DISCUSSION

The fact that the charge to spin ratio is about 50:1 leads us to conclude that the midgap absorption band as well as the doping induced IRAV lines originate from a spinless positively charged β-carotene. The existence of the absorption in the IRAV region is evidence that substantial geometry relaxation occurs upon doping. A possible structure of a positively charged spinless defect is shown in Fig. 1b and is denoted β-C^{++}. Two soliton-like defects are formed on the β-carotene skeleton by removing two electrons leaving the geometry relaxed. The resulting dication is doubly charged but spinless. The Coulomb repulsion between the two positive charges is balanced by the geometry relaxation. The single "midgap" electronic absorption band observed can naturally be explained by theoretical calculations as discussed above. We note at this point that the two solitons discussed here are equivalent to the

(positive) bipolaron case in an infinite conjugated polymer. In the latter case, two absorption bands are expected, but the intensity of the transition from the valence band to the upper bipolaron level is greatly reduced as the confinement is increased [10]. Thus, β-C^{++} may be thought of as a strongly confined bipolaron. Recent electron energy-loss spectroscopy studies [11] of iodine doped β-carotene also revealed a single midgap absorption line at 1.4 eV. However, when the q-dependence was compared to calculations based on an effective SSH-Hamiltonian, the midgap absorption was assigned to a polaron. This assignment is in contrast to the spinless state obsreved in our studies. Further studies are therefore needed to explain this apparent discrepancy.

The observed IRAV lines are in 1:1 correspondence with the resonantly enhanced Raman scattered (RRS) lines observed in β-carotene [12]. As in *trans*-$(CH)_x$, the IRAV lines are red-shifted relative to the RRS lines and may be thought of as amplitude modes which become IR active due to the charged defect [13, 14]. Following the procedure used for *trans*-polyacetylene [14], we have done an amplitude modes analysis of the RRS and IRAV lines of β-carotene and found a pinning parameter of $\alpha_p = 0.37$ for doped β-carotene, compared with $\alpha_p = 0.23$ in doped *trans*-$(CH)_x$ [14]. The larger pinning parameter found for β-carotene is in accord with the much less mobility of the charge expected for the finite size molecule. Furthermore, the "mass" of the soliton in *trans*-$(CH)_x$ could be inferred from the ratio of the integrated absorptions of the midgap to the IRAV bands, since the absorption is inversely proportional either to the band mass (for the midgap absorption) or to the kinetic mass of the soliton (for the IRAV absorption) [13]. Using the data of Figs. 3 and 4 we find that the ratio of the midgap to the IRAV integrated absorptions is five times larger in β-carotene than in *trans*-$(CH)_x$. This result indicates a heavier defect as expected due to its smaller spatial extent in β-carotene.

In addition, our ESR measurements show that there exist about 2% cation radicals, β-$C^{\bullet+}$, in our doped films. A suggested polaron-like structure for these radical cations is shown in Fig. 1c. The ESR linewidth of $\simeq$10 G observed here is typical to such radicals in conjugated molecules or in conjugated polymers where the structure is such that motional narrowing does not occur. The midgap absorption and IRAV are either overlapping those of the spinless defects or are too weak to be observed.

SUMMARY

We have shown that spinless charged soliton-like defects are formed, upon doping, in films of the conjugated molecule β-carotene. These defects resemble the solitons in trans-polyacetylene in that they show a single midgap transition, a set of IRAV modes and no spin. Calculations of the molecular and electronic structures show that the β-carotene dication is structurally similar to a pair of charged soliton defects having no spin, a single midgap absorption band and a set of IRAV lines.

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