## Molecular Crystals

## Photoconductivity of Carotenoids

R. J. Cherry [a] & D. Chapman [a]

[a] Molecular Biophysics Unit, Unilever Research Laboratory, The Frythe, Welwyn, Herts
Version of record first published: 21 Mar 2007.

PLEASE SCROLL DOWN FOR ARTICLE

# Photoconductivity of Carotenoids

R. J. CHERRY and D. CHAPMAN

Molecular Biophysics Unit, Unilever Research Laboratory, The Frythe, Welwyn, Herts.

**Abstract**—Further studies have been made of the photoconductivity of single crystals of all-*trans* β-carotene. Photoconductivity spectra have also been determined for the related molecules 15-15′ *cis* β-carotene, lycopene, β-apo-8′-carotenal, β-apo-8′-apocarotenoic acid ethyl ester and canthaxanthin, as well as a β-carotene glass. The results strongly indicate that a photoconductivity band which occurs well below the absorption edge in these materials is an intrinsic property of this type of molecule. The UV photoconductivity spectrum of 15-15′ *cis* β-carotene throws some doubt on previous theories concerning the production of free carriers in β-carotene following illumination by strongly absorbed light.

Carotenoids are materials which have considerable physical and biological interest. Semiconducting and photoconducting properties have been observed in compressed microcrystalline powders and in single crystals of β-carotene.[1, 2] The possible importance of carotenoids in mechanisms of electron transfer in biological systems has recently been reviewed by Dingle and Lucy.[3]

In a previous paper, we have described studies of some of the optical and electrical properties of all-*trans* β-carotene crystals.[2] An unusual feature of the photoconductivity of these crystals was the appearance in the excitation spectrum of a band at 13,300 $cm^{-1}$, which is at considerably lower energy than the absorption edge at about 18,000 $cm^{-1}$. In this paper we describe further experiments to determine whether this photoconductivity band is an intrinsic property of β-carotene, or whether it is due to some imperfection present in the crystal.

When β-carotene is melted, a mixture of stereo isomers is produced, which forms a glass on cooling.[1] Thus, such methods as zone

refining cannot be used as a means of improving the purity of the crystals. Therefore, in order to investigate possible impurity effects we have studied the photoconductivity of all-*trans* β-carotene crystals grown from various solvents, together with the photoconductivity of 15-15′ *cis* β-carotene crystals and the β-carotene glass.

If the low energy photoconductivity band in β-carotene is intrinsic, one might expect to observe it with other carotenoids. To investigate this possibility, we have studied the photoconductivity
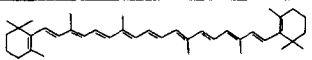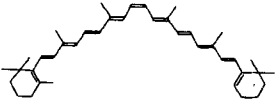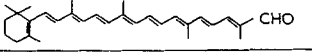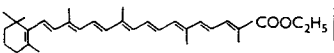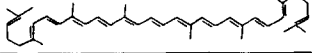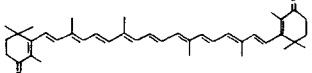
| Molecule | Structure | Crystal form and electrode arrangement |
|---|---|---|
| All *trans* β-carotene | | Platelets |
| 15—15′ cis β-Carotene | | Prismatic |
| β-Apo—8— carotenal | CHO | Platelets |
| β-Apo—8— carotenoic acid ethylester | COOC₂H₅ | Platelets |
| Lycopene | | Needles |
| Canthaxanthin | | Platelets |

Figure 1. Chemical structures and crystal forms of the various carotenoids.

of lycopene, β-apo-8′-carotenal, β-apo-8′-carotenoic acid ethyl ester and canthaxanthin. The structures of these molecules are shown in Fig. 1.

**Experimental**

A. CRYSTAL GROWTH

Single crystals of all-*trans* β-carotene were grown from benzene–methanol solution in a similar manner to that previously described.[2] Crystals were also grown from di-methyl formamide and from

tetrahydro-furan solution. A $\beta$-carotene "glass" was prepared from the melt in a similar way to that described by Rosenberg.[1] The starting material for these crystallisations was high purity microcrystalline all-*trans* $\beta$-carotene from two separate suppliers, Roche Products and E. Merck.

Single crystals of $\beta$-apo-8'-carotenal, $\beta$-apo-8'-carotenoic acid ethyl ester, lycopene and 15-15' *cis* $\beta$-carotene were obtained by slow cooling of a saturated benzene-methanol solution. Single crystals of canthaxanthin were grown from a chloroform-methanol solution. The forms of the crystals obtained are illustrated in Fig. 1. The lengths of the crystals were generally 1–3 mm and thicknesses of the order of $\frac{1}{10}$ mm. However, with lycopene only rather minute needle-shaped crystals were obtained. Crystals of 15-15' *cis* $\beta$-carotene and of $\beta$-apo-8'-carotenal sometimes grew as irregular shaped platelets of area several square millimetres, in addition to the forms illustrated. The starting material for these crystallisations were microcrystalline powders supplied by Roche Products. All crystals were stored at 0° C in the dark.

## B. PHOTOCONDUCTIVITY MEASUREMENTS

Previous measurements on all-*trans* $\beta$-carotene indicated that the photoconductivity spectra in air and *in vacuo* are similar.[2] The low energy photoconductivity band appears in both surface and bulk conductivity measurements. Most of the measurements reported here were made in air with two aquadag electrodes side by side on the surface of the crystal. The arrangement of the electrodes is shown in Fig. 1. The larger area crystals of $\beta$-apo-8'-carotenal and 15-15' *cis* $\beta$-carotene which were sometimes obtained, enabled us to measure the bulk photoconductivity in a direction perpendicular to the plane of the platelets. For these measurements, we used an evaporated silver film as a semi-transparent electrode and a guard ring to eliminate surface currents.

The spectral responses were recorded using a Hilger D 189 monochromator with a quartz prism. The wavelength drum of the monochromator was driven by a low speed motor so that a continuous recording of the spectrum could be made. A Xenon arc

was used as a light source for the region 30,000–15,000 cm$^{-1}$ and a tungsten lamp for the region 15,000–6,000 cm$^{-1}$. The photo-conductivity spectra are corrected for the emission spectra of the light sources. A D.C. voltage was applied to the crystal and photo-currents measured with a Keithley Model 417 Picoammeter. The variation of photocurrent with light intensity was measured using neutral density filters and a band pass filter to isolate the appro-priate region of the spectrum.

The temperature dependence of the bulk photocurrent was measured with all-*trans* $\beta$-carotene. The crystal was mounted in a dewar and measurements made *in vacuo*. The crystal was continu-ously illuminated by light from a 300 watt projector. As the emission of the lamp and the bulk photosensitivity of $\beta$-carotene both fell rapidly at wavenumbers greater than 16,000 cm$^{-1}$, the photocurrent observed was almost entirely due to the 13,000 cm$^{-1}$ photoconductivity band. It was therefore unnecessary to use a filter to isolate this region of the spectrum.

## Results

### A. PHOTOCONDUCTIVITY SPECTRA

The photoconductivity spectra of all-*trans* $\beta$-carotene, 15-15' *cis* $\beta$-carotene and $\beta$-carotene glass are shown in Fig. 2. The spectra have been corrected for the emission spectrum of the lamp, but as the actual photon flux was not measured, the photoconductivity is in arbitrary units. The different spectra have been adjusted in height to fit onto the same scale. Both the all-*trans* $\beta$-carotene supplied by Roche Products and that supplied by E. Merck gave similar results. The low energy photoconductivity of all-*trans* $\beta$-carotene crystals grown from three different solvents are shown in Fig. 3. These curves have been adjusted to give roughly the same peak height at 13,300 cm$^{-1}$.

The photoconductivity spectra of the other carotenoids examined are shown in Fig. 4. In the case of $\beta$-apo-carotenal, it was possible to make both bulk and surface photoconductivity measurements. With $\beta$-apo-carotenoic acid ethyl ester and canthaxanthin, the low

energy photoconductivity band is easily observable, but it is less intense, relative to the higher energy photoconductivity, than in β-carotene.
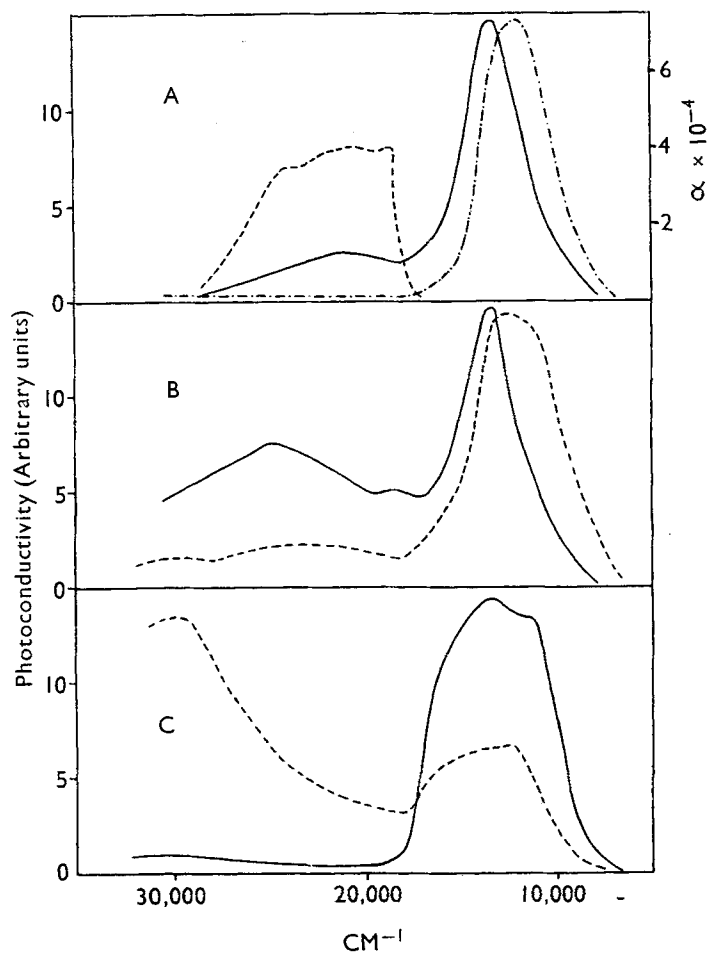


Figure 2. Photoconductivity excitation spectra of β-carotene. A, Bulk conductivity: ——— all-*trans* β-carotene; -·-·- 15-15′ *cis* β-carotene; ------ optical absorption (all-*trans*). B, Surface photoconductivity: ——— all-*trans* β-carotene; ------ 15-15′ *cis* β-carotene. C, β-Carotene glass: ——— surface electrodes; ------ sandwich cell.

With lycopene there was considerable difficulty in attaching electrodes to the crystals due to their minute size. Only in two cases did we succeed in making measurements, and these indicated that the dark conductivity was several orders of magnitude higher
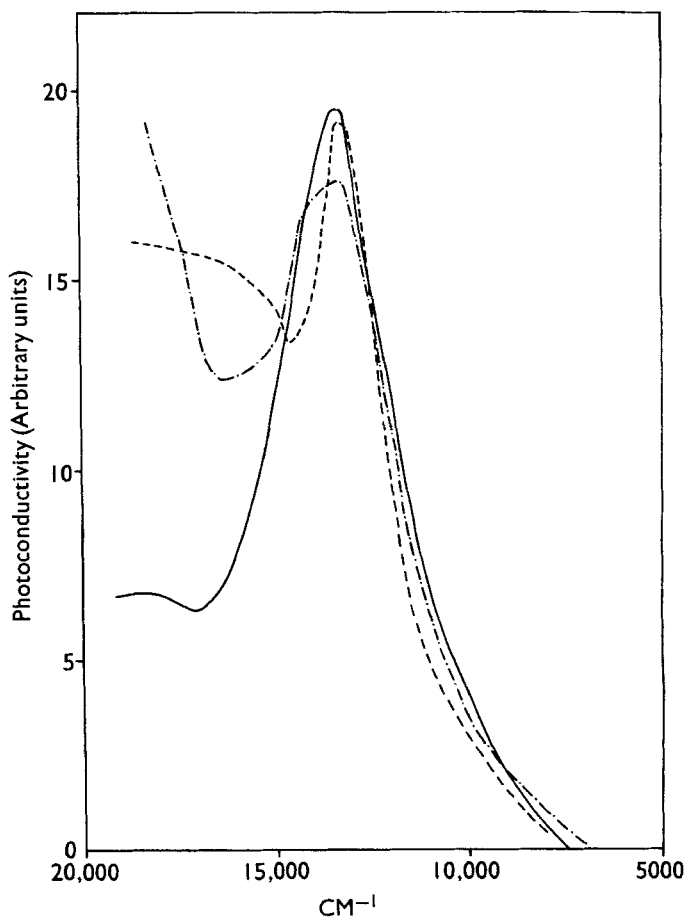
Figure 3. Surface photoconductivity of all-*trans* β-carotene crystals. ———— Crystals grown from benzene-methanol solution; ------ crystals grown from dimethyl formamide solution; ······ crystals grown from tetrahydrofuran solution.

than that of other carotenoids. The photosensivity over the whole
spectral range was very low and we were unable to obtain a spectral
response. It was just possible to show that photoconductivity did
occur in the range 10,000–13,000 cm$^{-1}$. As we could not obtain a
spectral response for the crystals, the spectrum shown in Fig. 4D is
of a compressed powder. At energies above 16,000 cm$^{-1}$ there is still
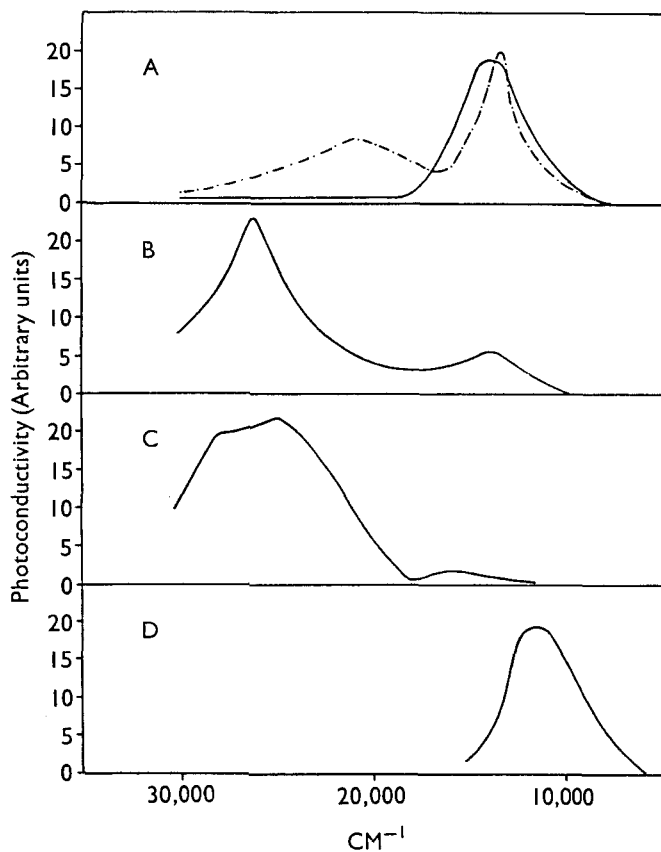


Figure 4. Photoconductivity excitation spectra.  A, $\beta$-apo-8′-carotenal:
—— bulk photoconductivity; ⋯⋯ surface photoconductivity. B, $\beta$-apo-
8′-carotenoic acid ethyl ester, surface photoconductivity. C, Canthaxan-
thin, surface photoconductivity. D, Lycopene, compressed powder.

17

a weak photoresponse, but large space charge effects prevented us from obtaining a meaningful spectral response in this region.

Whilst we have made no measurements of absolute photo-sensitivity, we noted that there were no great differences in the magnitudes of the low-energy photocurrents observed in the different isomers of $\beta$-carotene and in the various carotenoids. Typical photocurrents were in the range $10^{-11}$–$10^{-13}$ A. The currents could be maintained at a steady value for periods of at least several days. Electric field strengths were of the order of $10^4$ V/cm for bulk photoconductivity measurements and $10^3$ V/cm for surface measurements.

## B. OPTICAL ABSORPTION

Measurements of the optical absorption of crystals of all-*trans* and 15-15′ *cis* $\beta$-carotene, $\beta$-apo-8′-carotenal and $\beta$-apo-8′-caro-tenoic acid ethyl ester showed that the low energy photocon-ductivity band was in each case well below the absorption edge. With canthaxanthin, the photoconductivity band at 15,500 cm$^{-1}$ lies at an energy where there is still some absorption due to the tail of the lowest singlet $\pi$–$\pi^*$ transition.

Even in the thickest crystals available (all-*trans* $\beta$-carotene 0.6 mm thick), there was no indication of a separate absorption band in the region of the low energy photoconductivity band. This sets an upper limit of 0.3 for the absorption coefficient of the transition responsible for this band.

## C. VARIATION OF PHOTOCURRENT WITH LIGHT INTENSITY AND TEMPERATURE

The variation of surface photocurrent with light intensity for the various carotenoids is shown in Fig. 5. The results follow the equation

$$i = I^n$$

where $i$ is the photocurrent and $I$ the light intensity. The index $n$ was found to be between 0.5 and 1.0 in all cases.

The temperature dependence of the bulk photoconductivity of the 13,300 cm$^{-1}$ band of all-*trans* $\beta$-carotene *in vacuo* is shown in
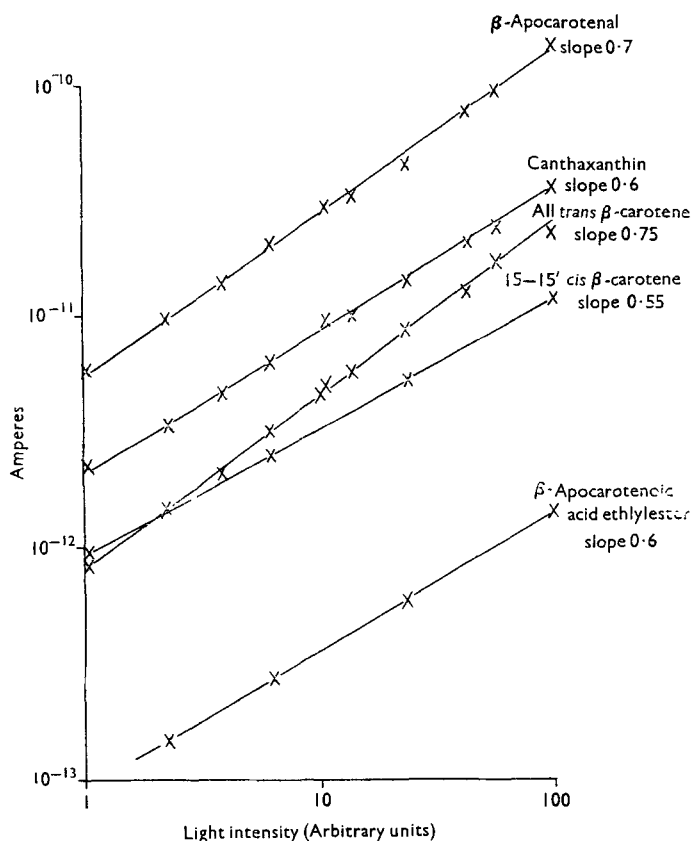


Figure 5. Variation of surface photocurrent with light intensity for the various carotenoids. Measurements were made in air at 20°C.

Fig. 6. The variation with temperature follows the exponential relationship

$$i = i_0 \exp \frac{-\Delta E}{kT}$$

where $i$ is the photocurrent, $i_0$ is a constant and $T$ the absolute temperature. The value of the activation energy $\Delta E$ was found to
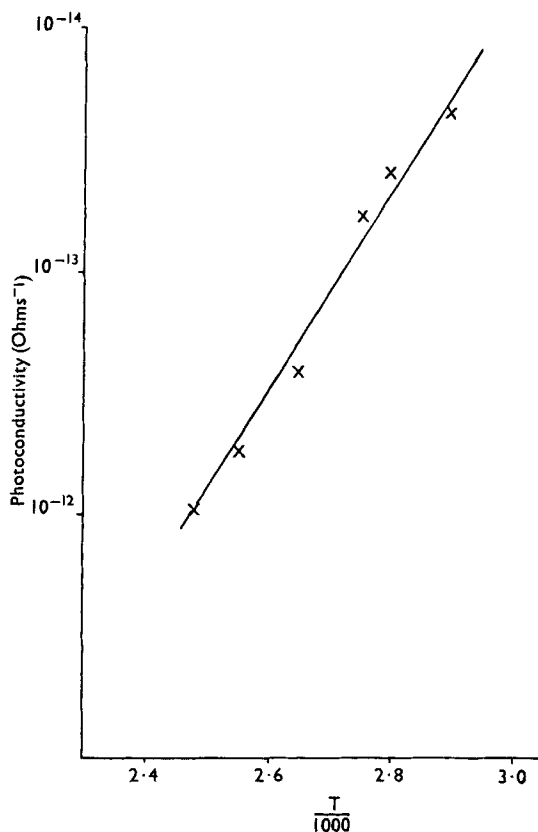
Figure 6. Variation with temperature of bulk photoconductivity of all-*trans* β-carotene *in vacuo*.

be close to 0.8 eV for three different crystals, the mean value being 0.78 eV.

D. MISCELLANEOUS OBSERVATIONS

(i) *Variation of photoconductivity with time*

In no case was any increase in photoconductivity with time observed. In fact, there is a tendency for the photosensitivity to decrease when the crystals are kept in air for several days. Attempts to hasten any chemical change by UV irradiation resulted merely in a slight decrease in the surface photoconductivity.

## (ii) *Electrode Effects*

In order to investigate possible electrode effects, two aquadag electrodes were painted onto the surface of an all-*trans* β-carotene crystal, so that their separation was about 3 mm. A narrow beam of red light, ½ mm in width, was focused onto the crystal between the electrodes. Little variation in the photocurrent was observed as the crystal was scanned by the light beam, i.e. the photocurrent was just as large when the electrodes were in the dark as when they were illuminated.

## (iii) *Effect of Oxygen*

Measurements were made of the effect of air and pure oxygen on the photoconductivity of all-*trans* β-carotene, 15-15′ *cis* β-carotene and β-apo-carotenal. Air and oxygen both reversibly increased the magnitude of the photoconductivity in agreement with Rosenberg's compressed powder measurements,[4] but produced no significant change in the form of the spectral response. In the case of all-*trans* β-carotene, the ratio of the photocurrent in air to the photocurrent *in vacuo* was 10 at 25,000 $cm^{-1}$ and 7.5 at 13,300 $cm^{-1}$. This measurement was of the surface photoconductivity at 57° C.

## (iv) *Double Beam Experiment*

With all-*trans* β-carotene measurement was made of the photoconductivity when the crystal was illuminated simultaneously with UV irradation and with red light. The photocurrent observed was slightly less than the sum of the photocurrents produced by the individual light beams.

## Discussion

### A. *Low Energy Photoconductivity*

We have consistently observed a low energy photoconductivity band in crystals of β-carotene grown from various solvents, in a β-carotene glass and in crystals of several other carotenoids. We can therefore eliminate the possibility of solvent contamination or lattice defects being responsible for the low energy photocon-

ductivity band. The possibility of electrode involvement is ruled out by the scanning light spot experiment. We have studied the effect of air and oxygen on all-*trans* β-carotene, and found that while these increase the photoconductivity, the magnitude of the increase is actually greater for the UV photoconductivity than for the low energy photoconductivity band. This is inconsistent with these gases being in any way responsible for the low energy photoconductivity.

If the low energy photoconductivity were due to the release of carriers from traps, simultaneous illumination with UV and red light might be expected to produce a photocurrent in excess of the sum of the photocurrents produced by the individual light beams.[5] Since this was not the case we conclude that traps are not involved in this way. The ability of the β-carotene to sustain a steady photocurrent at 13,300 cm$^{-1}$ over long periods also supports this conclusion.

Since carotenoids are rather unstable, it is possible that the observed photoconductivity arises following a small amount of permanent oxidation or decomposition of the crystals. However, no increase of photosensitivity with time is observed, even after UV irradiation.

There remains the possibility that an impurity which is present in all our starting materials is responsible for the low energy photoconductivity. The various carotenoids do, in fact, have rather similar synthetic pathways.[6] However, the precursors in the various syntheses all have equal, or shorter, chain lengths to β-carotene, and are therefore not expected to absorb at longer wavelengths. A preliminary attempt to incorporate one of these precursors, 15-15'-dehydro-β-carotene, into crystals of all-*trans* β-carotene, did not produce any enhancement of the low energy photoconductivity. Thin layer chromatographic tests of all-*trans* and 15-15'*cis*-β-carotene did not reveal any impurities in these materials. It was concluded that any impurity concentrations present were certainly much less than the 1–3 % concentrations used by Almeleh and Harrison[7] to produce impurity photoconductivity in tetracene.

We therefore consider it most likely that the low energy photo-conductivity band is an intrinsic property of $\beta$-carotene and of several related molecules. The shape of the band in the different forms of $\beta$-carotene provides some additional evidence for this conclusion. The photoconductivity peak is shifted from 13,300 $cm^{-1}$ in the all-*trans* to about 12,000 $cm^{-1}$ in the 15-15' *cis* isomer. If we are observing an intrinsic transition, whose energy varies from one isomer to another, we might expect in the glass, which is a mixture of many stereo-isomers, to see a broad, rather smeared out photoconductivity band. This is, in fact, what is observed. The surface phtoconductivity of the glass still shows a maximum at 13,300 $cm^{-1}$. This is reasonable since the mixture of stereo-isomers, produced by melting, contains $\sim 33\%$ of the all-*trans* isomer.[8]

The processes most likely to account for the low energy photo-conductivity band are:

    (a) Production of free carriers following excitation to a triplet state.

    (b) Production of free carriers following excitation to a charge-transfer state.

    (c) Direct excitation to a conduction band.

All these transitions would be very difficult to detect in absorption, but could well provide enough free carriers to produce appreciable photoconductivity.

We have already discussed the possible involvement of the triplet state in the photoconductivity of all-*trans* $\beta$-carotene.[2] The energy of the lowest triplet state in $\beta$-carotene is unknown. Lewis and Kasha[9] observed phosphorescence in lycopene and suggest that the lowest triplet state for this molecule lies at an energy 18,300 $cm^{-1}$ above the ground state. If this is the case, the photoconductivity band at 12,000 $cm^{-1}$ observed with lycopene could not arise from singlet-triplet transitions. However, it is to be noted that very little phosphorescence was observed in a freshly prepared solution of all-*trans* lycopene. Stronger emission was observed only after allowing the solution to stand for some time; the phosphorescent

spectra obtained becoming increasingly complex with time. As the reason for this is not properly understood, there must be some reservation about identifying the phosphorescent bands with the lycopene triplet state.

There has been considerable interest in charge-transfer states in monomeric molecular crystals of late,[10-13] although, apart from tetracene and anthracene,[11] there is little experimental evidence for their location. The chief difficulty in identifying the low energy photoconductivity band in carotenoids with a transition to a charge-transfer state is that one would expect a rapid radiationless decay of the lowest singlet excitons to this state.[12] Thus, even if one assumes that free carriers are produced most efficiently from charge-transfer excitons, it is not clear why the photoconductivity is so weak in the region of the singlet absorption band.

If the low energy photoconductivity is due to direct excitation to a conduction band, then the photoconductivity activation energy of 0.78 eV measured for all-*trans* β-carotene would have to be due to a thermally activated mobility such as is found in transition metal oxides.[14] In this case, one would expect the photoconductivity activation energy to be at least this value irrespective of how the free carriers are produced. Rosenberg,[15] however, reports an activation energy of 0.37 eV for the UV photoconductivity of a compressed powder of all-*trans* β-carotene. Hence this suggests that direct excitation to a conduction band does not account for the low energy photoconductivity observed with this material.

We have previously shown that the bulk photoconductivity of all-*trans* β-carotene is proportional to the square root of the light intensity.[2] The surface photocurrents of the different carotenoids are also found to vary sub-linearly with light intensity in the low energy band. This indicates that the production of free carriers is in every case a monomolecular process.

Further experiments are clearly needed to establish the nature of the transition responsible for the low energy photoconductivity observed in carotenoids. Meanwhile we note that photoconductivity bands occurring below the absorption edge have occasionally been reported in other molecular crystals.[5, 16-18] Apart from anthracene

where a weak photoconductivity band has been correlated with absorption to the triplet state,[18] it has not generally been possible to reach any firm conclusions about the nature of these bands, and in some instances there is evidence that they are due to impurities.[5, 16] The photoconductivity of carotenoids is of particular interest since in all the molecules investigated it appears that a weak transition plays an important role in the production of free carriers. A further study of these molecules may lead to a greater understanding of the energy levels which occur in molecular crystals.

## B. *UV Photoconductivity*

Some variations are observed in the relative magnitudes of the UV and the low energy photoconductivity band, both in crystals of all-*trans* β-carotene grown from different solvents and amongst the different carotenoids. These variations could be due to differences in the efficiency of free carrier formation or to differences in trapping and recombination properties. The latter might be expected to have a greater effect on the UV photoconductivity where the free carriers are produced in a thin layer close to the surface of the crystal.

The UV photoconductivity spectrum observed in the β-carotene glass sandwich cell is in agreement with Rosenberg's results[19] in that there is a peak at about 29,000 cm$^{-1}$. This is the energy of the "*cis*" absorption, a π–π* transition which is symmetry forbidden in the all-*trans* isomer, but allowed in the *cis* isomers. Rosenberg concludes that free carriers are most efficiently produced in β-carotene following transitions to this state. He later reported that the spectrum of a powder of the 15-15′ *cis* isomer was similar to that of the glass.[15] However, our measurements with 15-15′ *cis* β-carotene single crystals give no indication of a peak in the spectral response at 29,000 cm$^{-1}$. There is also little sign of a peak at this energy in the surface photoconductivity spectrum of the glass. It may therefore be that the agreement between the photoconductivity peak and the *cis* absorption which has been observed is coincidental, especially bearing in mind that photoconductivity maxima in regions of strong absorption may be shifted in energy by

recombination processes[20] and may also be dependent on electrode arrangement and electric field strength.[21]

## Conclusions

A low energy photoconductivity band has been consistently observed in all-*trans* and 15-15' *cis* β-carotene and in β-carotene glass as well as in several related carotenoids. We conclude that this band is very probably an intrinsic feature of the photoconductivity of these materials. It is not yet possible to decide between several transitions which could account for the photoconductivity at these low energies.

The UV photoconductivity spectra of 15-15' *cis* β-carotene crystals throws doubt on a previous suggestion that transitions to the "*cis*" state are much more efficient than transitions to the lowest singlet state in producing free carriers in β-carotene.

## Acknowledgments

### REFERENCES

1. Rosenberg, B., in *Electrical Conductivity in Organic Solids*, Interscience Publishers, 1961, p. 291.
2. Chapman, D., Cherry, R. J., and Morrison, A., *Proc. Roy. Soc.* (1967) (in press).
3. Dingle, J. T. and Lucy, J. A., *Biol. Rev.* **40**, 422 (1965).
4. Rosenberg, B., *J. Chem. Phys.* **34**, 812 (1961).
5. Almeleh, N. and Harrison, S. E., *J. Phys. Chem. Solids* **27**, 893 (1966).
6. Isler, V. O., Rüegg, R., and Schudel, P., *Chimia* **15**, 208 (1961).
7. Almeleh, N. and Harrison, S. E., *J. Phys. Chem. Solids* **26**, 1571 (1965).
8. Zechmeister, L., *Progress in the Chem. of Organic Natural Products* **18**, 223 (1960).
9. Lewis, G. N. and Kasha, M., *J. Am. Chem. Soc.* **66**, 2100 (1944).
10. Choi, S. I., Jortner, J., Rice, S. A., and Silbey, R., *J. Chem. Phys.* **41**, 3294 (1964).
11. Pope, M., Burgos, J., and Giachino, J., *J. Chem. Phys.* **43**, 3367 (1965).
12. Kearns, D. R., *J. Chem. Phys.* **41**, 581 (1964).
13. Berry, R. S., Jortner, J., Mackie, J. C., Pysh, E. S., and Rice, S. A., *J. Chem. Phys.* **42**, 1535 (1965).
14. Morin, F. J., *Phys. Rev.* **93**, 1195 (1954).

15. Rosenberg, B., *J. Chem. Phys.* **34**, 63 (1961).
16. Reucroft, P. J., Rudyj, O. N., Salomen, R. E., and Labes, M. M., *J. Chem. Phys.* **43**, 767 (1965).
17. Day, P. and Williams, R. J. P., *J. Chem. Phys.* **37**, 567 (1962).
18. Sharp, J. H. and Schneider, W. G., *J. Chem. Phys.* **41**, 3657 (1964).
19. Rosenberg, B., *J. Chem. Phys.* **31**, 238 (1959).
20. Kommandeur, J. and Schneider, W. G., *J. Chem. Phys.* **28**, 582 (1958).
21. Lyons, L. E. and Mackie, J. C., *J. Chem. Soc.* 5186 (1960).