The S_1 and T_1 Energy Levels of All-*trans* β-Carotene

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Reflectance spectroscopy of all-*trans* β-carotene in the zeolite, ZSM-5, allows the forbidden $S_0 \rightarrow S_1$ transition ($1\,^1A_{g-} \rightarrow 2\,^1A_{g-}$) to be detected; hence the S_1 energy level is determined for the first time and an estimate of the T_1 energy level made.

Carotenoids are a class of compounds that, together with their oxygenated derivatives, play an important role in a wide range of biological systems.[1] For example, β-carotene acts as both a light-harvester and a photo-protector in photosynthesis, it is used as a drug to treat the hereditary disease, erythropoietic protoporphyria, is belived to have anticancer properties and is widely used as a food colourant. Despite the importance of carotenoids, the precise nature of the electronic excited states are not well understood and neither the energy level of the first excited singlet state, $S_1(2^1A_{g-})$ nor the lowest triplet state, T_1, is established.

The 2^1A_{g-} state may well be pivotal in the role of β-carotene in photosynthesis (and of bacterial carotenoids in bacterial photosynthesis), particularly with respect to energy transfer to chlorophylls in the antenna system. In this communication we report, for the first time, the direct detection of the symmetry forbidden $1^1A_{g-}(S_0)$ to $2^1A_{g-}(S_1)$ absorption band by reflectance absorbance spectroscopy and thus the determination of the 2^1A_{g-} energy level. Also, an estimate of the lowest triplet energy level 1^3Bu^+ (T_1) of β-carotene arises from the valance bond[2] description of the 2^1A_{g-} state wavefunction. In this model it is suggested that the triplet energy should be one-half that of the 2^1A_{g-} state.

In this study we have introduced all-*trans* β-carotene into the zeolite ZSM-5. This zeolite of composition $Na_n(Al_nSi_{196-n}O_{192})\cdot xH_2O$ (x = *ca.* 16) contains straight channels parallel to the unit cell b axis which is ~19.9 Å in length (and also sinusoidal channels parallel to the a axis). These channel cross-sections are 5.3 × 5.6 Å and 5.1 × 5.5 Å, respectively. The zeolite was dehydrated by heating under vacuum (10^{-5} atm) to 350 °C slowly (in 10° steps) allowing the pressure to fall at each stage. Subsequently, it was maintained at 350 °C for 12 h. The vacuum was released and dry air passed over the zeolite (at 350 °C) for 4 h to remove any absorbed hydrocarbons. The sample was then placed under vacuum (10^{-5} atm) for a further 6 h. The β-carotene, in trimethylpentane (as solvent with dimensions greater than those of the zeolite channel) was then loaded onto the zeolite in a helium atmosphere. Subsequently, the zeolite/β-carotene was washed until no further β-carotene could be removed. After drying, the absorption spectra were obtained by reflectance spectroscopy using a Perkin-Elmer Lambda 9 spectrophotometer. Fig. 1 shows the spectra of the zeolite alone (a) and of the zeolite in which the β-carotene is encapsulated (b). As can be seen for Fig. 1 (b) there is a distinct new band at 700 ± 20 nm. If this is assigned as the $S_0 \rightarrow S_1$ ($1^1A_{g-} \rightarrow 2^1A_{g-}$) transition the energy of the 2^1A_{g-} state is 14 200 ± 400 cm^{-1} (170 ± 5 kJ mol^{-1}) and the lowest triplet (T_1) estimated, as described above, to be 85 ± 3 kJ mol^{-1}. It should be noted that the new band is not observed in the reflectance spectra of either solid β-carotene or β-carotene adsorbed onto silica and is in the correct spectral region predicted for the S_1 energy level.

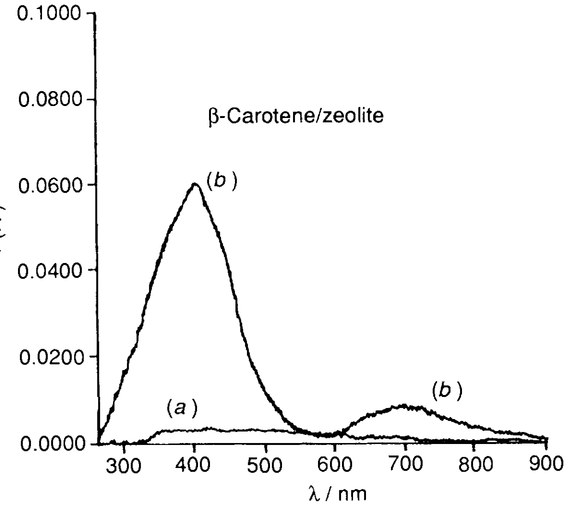

Fig. 1 The reflectance spectrum of all-*trans* β-carotene in ZSM-5 zeolite plotted as the Kubelka–Munk function, F(R) against wavelength, eqn. (1).

$$F(R) = \frac{(1-R)^2}{2R} = \frac{K}{S} \qquad (1)$$

Where R is the reflectance, K the absorption coefficient and S the scattering coefficient.

In ethanol the $1^1A_{g-} \rightarrow 1^1B_u$ transition in all-*trans* β-carotene shows peaks at ~440, 465 and 505 nm. In *cis* β-carotene there is an additional, so-called '*cis*', peak around 330 nm. The transition responsible for the *cis* peak ($1^1A_{g-} \rightarrow 1^1A_{g+}$) is singly forbidden in all-*trans* β-carotene, and it is suggested that like the doubly forbidden $1^1A_{g-}{*}\ 2^1A_{g-}$, it will become, at least partially, allowed in the (asymmetric) zeolite environment and hence in this case be very intense. Fig. 1 shows that as well as the doubly forbidden $1^1A_{g-} \rightarrow 2^1A_{g-}$ peak at 700 nm we also detect a strong, broad band with $\lambda_{max} \approx 402$ nm, extending from about 300 to 500 nm. This may well be due to the unresolved combination of the $^1A_{g-} \rightarrow {^1B_u}$ plus the, now allowed, $1^1A_{g-} \rightarrow 1^1A_{g+}$ transitions. Another possible factor which affects this λ_{max} is that bonds due to the $1^1A_{g-} \rightarrow 1^1B_u$ transition are well known to be very solvent dependent, unlike the $1^1A_{g-} \rightarrow 2^1A_{g-}$ transition.

β-Carotene has 11 conjugated double bonds (n) and for polyenes with fewer double bonds than β-carotene ($n \leq 8$) it is possible to observe the $1^1A_{g-} \leftrightarrow 2^1A_{g-}$ transition, it is only when $n > 8$ that this transition is lost and only the $1^1A_{g-} \leftrightarrow 1^1B_u$ transition observed. However, extrapolation of the $1^1A_{g-} \leftrightarrow 2^1A_{g-}$ transition with respect to n, the number of conjugated double bonds, for the α,ω-dimethylpolyenes (361 for tetraene, 412 for pentaene, 468 for hexaene, 514 for heptaene and 560 nm for octaene),[3] leads to an estimate of the $S_0 \leftrightarrow S_1$ transition at *ca.* 710 nm, very close to our observed band at 700 nm with the extrapolated value being more or less independent of environment. However, this extrapolation and our direct measurement predicts a 2^1A_{g-} energy level markedly lower than that arising from the Raman measurements (~18 000 cm^{-1}).[4,5] Since the 1^1B_u energy level (483 nm) corresponds to 20 700 cm^{-1}, our observation suggests an energy gap of ~6 500 cm^{-1} for the 1^1B_u–2^1A_{g-} separation, markedly larger than that of ~3 470 cm^{-1} predicted from the Raman data. Indeed, more recently, it has been suggested, from resonance Raman data, that such a technique is not able to reliably determine the $1^1A_{g-} \leftrightarrow 2^1A_{g-}$ transition.[6]

For longer chain carotenoids it would be expected that the S_1 and T_1 energy levels would be lower than of β-carotene. Using the same procedure we have obained decapreno-β-carotene ($n = 15$) in the zeolite and its exhibits a new band at about 820 nm corresponding to an S_1 energy level of 146 kJ mol^{-1} and an estimated T_1 energy level of 73 kJ mol^{-1}.

We have previously reported[7] the rates of reaction of singlet oxygen with β-carotene and longer polyenes such as dodecapreno β-carotene. These rate constants are consistent with a β-carotene lowest triplet energy very close to that of singlet oxygen in agreement with the value of 85 kJ mol^{-1} given above.

The environment of short polyenes on zeolites has shown that an interaction between the zeolite and the polyene occurs and leads to the formation of the radical cation of the polyene. We do not observe the radical cation of β-carotene but we suggest that the environment and interaction of the β-carotene in the zeolite is such that the symmetry selection rule breaks down so the $1^1A_{g-} \rightarrow 2^1A_{g-}$ transition is observed.

The S_1 energy level of all-*trans* β-carotene is 170 ± 5 kJ mol^{-1}, which is just below the S_1 energy level of chorophyll a. The T_1 energy level of all-*trans* β-carotene is ~85 ± 3 kJ mol^{-1} which is just below that of singlet oxygen.

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