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RESONANCE RAMAN SPECTRA OF ALL-*TRANS* AND 15,15′-*CIS*-β,β-CAROTENES

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The Raman spectra of all-*trans* and 15,15′-*cis*-β,β-carotenes were observed using various laser lines for excitation. Differences, not dramatic but significant, were found between the spectra of the two isomers. With ultraviolet excitations both isomers gave a few bands in the C=C stretching region, whereas a single band was observed with visible excitations.

The resonance Raman spectra of the all-*trans* isomer of β,β-carotene (hereafter abbreviated as β-carotene) excited with the laser lines in the 440∿520-nm region have been studied by many authors.[1-4] The mechanism of resonance effect is mostly understood in terms of the structural difference between the ground (^1A_g) and the first excited (^1B_u) states and the overlap integrals of the vibrational wavefunctions in these two electronic states.[3,4] As for the other isomers of β-carotene, on the other hand, only a paper has reported the resonance Raman spectrum of the 15,15′-*cis* (abbreviated as 15-*cis*) isomer.[5]

It is well known that a carotenoid having a *cis* double bond exhibits an absorption called the '*cis*-peak' at a wavelength about 140 nm below the absorption maximum of the longest wavelength of the corresponding all-*trans* isomer. The primary purpose of our present study is to examine the differences between the resonance Raman spectra excited using ultraviolet laser lines resonant with the *cis*-peak and those obtained with the 440∿520-nm excitations. As shown in Fig. 1, 15-*cis*-β-carotene has a fairly strong *cis*-peak at 340 nm, whereas only a very weak absorption is seen in this region of the all-*trans* spectrum. The absorption bands of both isomers in the visible region are quite similar, though the peaks of 15-*cis* are a little shorter in wavelength and weaker in intensity, reflecting the situation that the double-bond conjugation is less extended in this isomer. For both isomers the transition moment of the visible absorption is parallel to the long

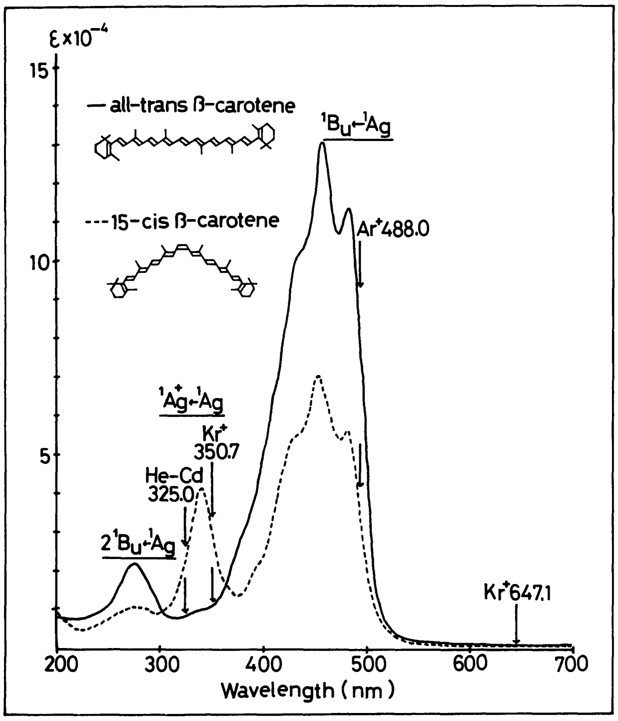


Fig. 1. Absorption spectra of all-*trans* and 15-*cis*-β-carotenes in the ultraviolet and visible regions. (——), all-*trans*; (---), 15-*cis*.

The arrows indicate the positions of the laser lines used for Raman measurements.

axis of the respective molecule (*i.e.*, the chain direction itself for all-*trans* and the line linking one end with the other for 15-*cis*), while the *cis*-peak has a transition moment perpendicular to the long axis.[6-8] If the notations for the all-*trans* system are retained in the case of 15-*cis*, the *cis*-peak corresponds to the transition $^1A_g^+ \leftarrow {}^1A_g$ which is forbidden in all-*trans*. Another absorption around 280 nm is assigned to the transition $2^1B_u \leftarrow {}^1A_g$.[9,10]

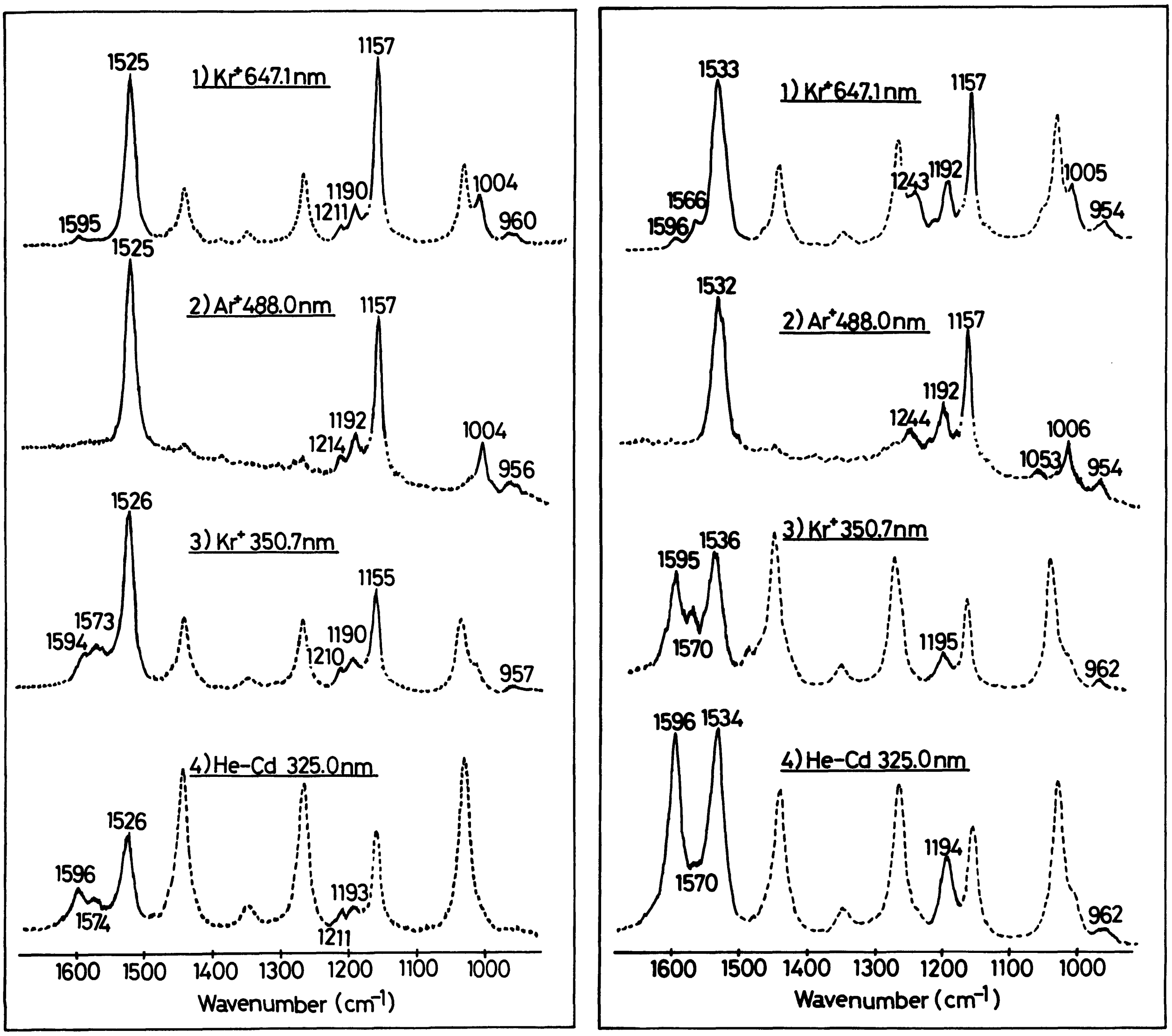
In Fig. 2 are shown the Raman spectra of all-*trans* and 15-*cis*-β-carotenes in cyclohexane excited with the 647.1(Kr^+), 488.0(Ar^+), 350.7(Kr^+), and 325.0(He-Cd)-nm laser lines. The rotating-cell technique was employed for observing the spectra in this figure. Irradiation of the laser lines, particularly the ultraviolet lines, was found to induce some photoreactions. Therefore, the absorption spectra were measured before and after each Raman measurement in order to ensure that no appreciable reaction occurred in the sample during the laser irradiation. The Raman spectra observed using the flow technique[11] (which is useful for suppressing the effects of photoreactions) were essentially the same as those in Fig. 2. Further, the Raman spectra obtained for the two isomers of β-carotene in a low-temperature glass (ethyl ether 5: isopentane 5: ethanol 2, 77K) confirmed that the spectra shown in Fig. 2 were free from photoreaction products.

The following points are noted in Fig. 2.

(1) Although the spectra of 15-*cis* observed with the 647.1- and 488.0-nm excitations resemble those of all-*trans* obtained under the same conditions, there are some features which clearly distinguish these two isomers. The frequency of the strong C=C stretching band of 15-*cis* (1532 cm^{-1}) is higher by about 7 cm^{-1} than

that of all-*trans* (1525 cm^{-1}). The same result was recently reported by Lutz *et al.*[5] The two weak bands at 1244 and 1053 cm^{-1} are characteristic of 15-*cis*.

(2) In the spectrum of 15-*cis* excited with 350.7-nm line a strong band at 1595 cm^{-1} and a weak one at 1570 cm^{-1} are observed in addition to a strong band at 1536 cm^{-1}. The spectrum obtained with the 325.0-nm excitation has similar features but the intensity of the 1570-cm^{-1} band is weaker. The intensities of 1595- and 1570-cm^{-1} bands (and possibly the 1536-cm^{-1} band also) are considered to be enhanced in resonance with the *cis*-peak. Prolonged irradiation of 350.7-nm line on the



(a) (b)

Fig. 2. Raman spectra of all-*trans* and 15-*cis*-β-carotenes observed with 647.1-, 488.0-, 350.7-, and 325.0-nm excitations. (a), all-*trans*; (b), 15-*cis*. A rotating-cell was used. The parts indicated with broken curves are due to the solvent (cyclohexane).

15-*cis* sample caused simultaneous decreases in the intensities of the *cis*-peak absorption and the 1595- and 1536-cm^{-1} bands.

(3) In the spectra of all-*trans* excited with the 350.7- and 325.0-nm lines weak bands are observed at 1594 and 1573 cm^{-1}. This is somewhat surprising because all-*trans* has only an extremely weak absorption in the 350∿320-nm region which is assigned to the forbidden transition. Since the 1594-cm^{-1} band becomes stronger with the 325.0-nm excitation, the preresonance effect with the absorption at 280 nm may be a factor which enhances the intensity of this band.

(4) Thus, the band at 1595 cm^{-1} cannot be regarded as a band characteristic of 15-*cis*. However, the intensity of the 1595-cm^{-1} band relative to the intensities of the other bands is much stronger for 15-*cis* than for all-*trans* with the near-ultraviolet excitations.

(5) For both 15-*cis* and all-*trans* the weak bands in the 1600∿1560-cm^{-1} region can be observed with the 647.1-nm excitation (an off-resonant condition). With the 488.0-nm excitation these bands are not observed because of the rigorous resonance with the strong visible absorption which enhances the intensity of the 1532-cm^{-1} band (15-*cis*) or the 1525-cm^{-1} band (all-*trans*).

More detailed description of the experimental results and the assignments of the bands between 1600 and 1560 cm^{-1} will be reported elsewhere.

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