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TRANSIENT RAMAN SPECTRA OF ALL-TRANS- AND 9-CIS-RETINAL IN THE EXCITED TRIPLET STATE

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Transient Raman spectra of all-trans- and 9-cis-retinal in the excited triplet state have been obtained using a Q-switched Nd:YAG laser. It has been found that the triplet Raman spectra of these two isomers are identical within the limit of experimental uncertainty suggesting the same triplet state in all-trans- and 9-cis-retinal.

Electronically excited states of polyenes are of particular importance in connection with the mechanism of the cis-trans photoisomerization, which is thought to trigger many photobiological reactions. In these five years, transient resonance Raman spectroscopy has been applied to all-trans-β-carotene,[1,2] other carotenoids,[3,4] and all-trans-retinal[5,6] and the vibrational characterization of their lowest excited triplet states (T_1) has been made. Recently, Wilbrandt and Jensen[7] extended the study to 15-cis-β-carotene. They found that the T_1 Raman spectrum of the 15-cis isomer was essentially the same as that of all-trans and suggested that the dominant product of the triplet-triplet energy transfer from naphthalene to all-trans- and to 15-cis-β-carotene was the same triplet species twisted around the 15,15'-C=C double bond. In this regard, it is interesting to see whether or not a similar phenomenon occurs in retinal, for which the T_1 state can be efficiently produced by the intersystem crossing with the lowest excited singlet state S_1. The present letter is a preliminary report on a comparative study of the triplet Raman spectra of all-trans and mono-cis isomers of retinal.

All-trans-retinal was purchased from Kanto Chemical Co., Inc. The 9-cis sample was a gift from F. Hoffmann-La Roche & Co. Both samples were used without further purification. Transient Raman spectra were obtained with the apparatus reported previously.[8] The third harmonic (355 nm) of a Q-switched Nd:YAG laser (Quanta-Ray DCR-2A) was used to pump retinal to S_1 and the transient Raman scattering from T_1 populated by the subsequent intersystem crossing was probed with the second harmonic pulse (532 nm) delayed by 19 ns. Methanol solutions with 4×10^{-4} M (all-trans) and 1×10^{-4} M (9-cis) concentrations were used with a jet flow technique.[8] The sample solution (50 ml) was circulated (about 15 times during one measurement) but the effect of the photoisomerization during the measurement was negligibly small (the portion of irradiated molecules less than 10^{-2}).

The obtained Raman spectra of all-trans-retinal are given in Figs. 1-a and 1-b. The former was observed with both the pump and probe beams incident on the

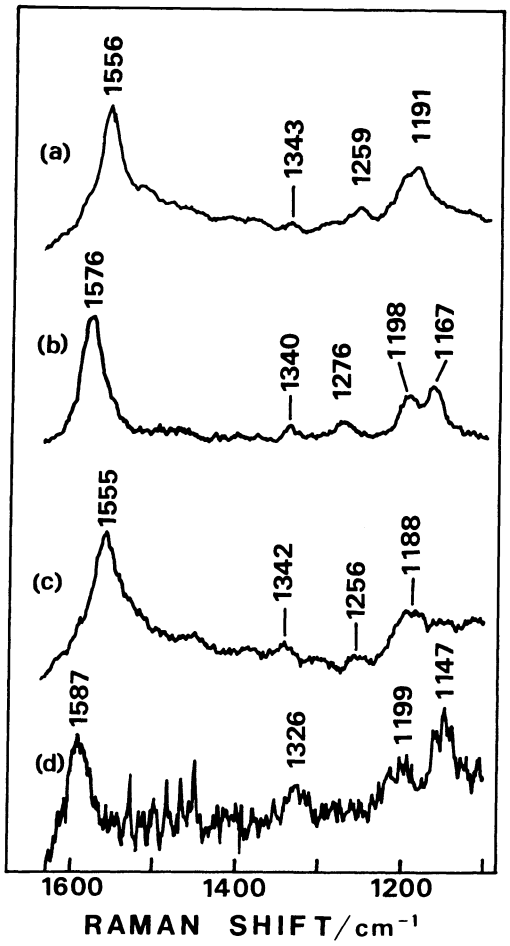

Fig. 1. Raman spectra of all-trans-retinal obtained with (a) pump and probe beams, (b) probe beam only, and of 9-cis-retinal obtained with (c) pump and probe beams, (d) probe beam only. The solvent bands were subtracted in each spectrum.

sample, whereas the latter was obtained without the pump beam. The spectra in 1-a and 1-b agrees with the T_1[5,6] and S_0[9] spectra of all-trans-retinal reported previously. The same set of experiments was repeated for 9-cis-retinal. The resultant spectra are given in Figs. 1-c and 1-d. Because of the high fluorescence background due to impurities, the S/N ratios in the 9-cis spectra are much worse than in the all-trans. Nevertheless, the spectrum in 1-d is distinctly different from 1-b and is in full agreement with the S_0 spectrum of 9-cis-retinal.[9] On the other hand, all the features in the spectrum in 1-c are found in 1-a and these two spectra are identical within the limit of experimental uncertainty. It is known that the $T_n \leftarrow T_1$ absorption spectra of 9-cis and all-trans-retinal are similar to each other.[10] This means that the pre-resonance effects on the triplet Raman intensities in 9-cis and in all-trans should be comparable and hence excludes the possibility that a small amount of all-trans impurity gives rise to the main features in Fig. 1-c because of much stronger resonance effects. We therefore conclude that the triplet state produced from 9-cis-retinal gives the same Raman spectrum as that produced from all-trans. Presumably, the photoexcitation of all-trans- and 9-cis-retinal results in the same triplet state, which can be a single triplet conformer or an equilibrated mixture of more than one species with different conformations. A further study including all the other mono-cis isomers is now in progress.

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