PICOSECOND TRANSIENT NEAR-INFRARED EXCITED RAMAN SPECTRA OF β-CAROTENE: DYNAMICS AND SOLVENT EFFECTS ON THE IN-PHASE C=C STRETCHING MODE IN THE S₂ (1Bu⁺) EXCITED STATE

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Abstract: By using a near-infrared excited Raman spectrometer with about 3.3 ps time resolution, we succeeded in obtaining picosecond transient Raman spectra of β-carotene in the S₂ (1Bu⁺) excited state. The in-phase C=C stretching mode of β-carotene in the S₂ state was observed at about 1550 cm⁻¹. The solvent effects on this band are discussed in comparison with the previous results on the S₀ (1Ag⁻) ground state and the S₁ (2Ag⁻) excited state.

Carotenoids play an important role in the light–harvesting function in photosynthesis. All-trans-β-carotene (β-carotene) is a typical carotenoid with a linear polyene structure that has pseudo C₂h symmetry. The S₀ ground state of β-carotene has 1Ag⁻ symmetry. The lowest singlet excited state, S₁ (2Ag⁻), is therefore optically forbidden. The lowest optically active state is the S₂ (1Bu⁺) state. The relaxation kinetics in carotenoids have been extensively investigated by using time-resolved spectroscopy. The photogenerated S₂ (1Bu⁺) state converts to the S₁ (2Ag⁻) state within 100 – 350 fs, and the lifetime of the S₁ (2Ag⁻) state is several picoseconds. Recently, Yoshizawa and co-workers reported that the S₂ (1Bu⁺) state of β-carotene has a transient absorption in the near-infrared region over 1000 nm [1]. In the present study, we measured the transient Raman spectra of β-carotene in the S₂ (1Bu⁺) state in resonance with this near-infrared transient absorption. Attention has been focused on the solvent effect on the Franck–Condon–active in-phase C=C stretching mode, which appears strongly in the resonance Raman spectra. In comparison with the solvent effects on the C=C stretching modes in the S₁ (2Ag⁻) and S₀ (1Ag⁻) states [2], the vibronic coupling mechanism [3] and the molecular structure in the S₂ (1Bu⁺) state are discussed.

The 1064-nm light (repetition rate 1 kHz) from a picosecond optical parametric generator and amplifier excited by the fundamental output (wavelength 775 nm) from a picosecond Ti:sapphire regenerative amplifier was used to probe the Raman scattering from the excited sample by the pump-probe technique. The second harmonic output (wavelength 388 nm) from the Ti:sapphire regenerative amplifier was used to excite the sample. The cross-correlation time between the pump and probe pulses was about 3.3 ps. Raman-scattered radiation passed through holographic notch filters was steered to a dispersive spectrometer with an InGaAs array detector. Solutions of β-carotene in six solvents (benzene, tetrahydrofuran, cyclohexane, acetone, n-hexane, and n-pentane) were circulated through a flow cell for the transient Raman measurements.

Figure 1 shows picosecond transient Raman spectra obtained from the six kinds of β-carotene solutions at a delay time of 0 ps between the pump and probe laser pulses. A strong Raman band is observed at about 1550 cm⁻¹ in addition to some bands in the 1300 – 1100 cm⁻¹ region. Since the temporal behavior of the 1550-cm⁻¹ band is in good agreement with that of the near-infrared transient absorption due to the S₂ (1Bu⁺) state reported in ref [1], these spectra are assignable to the S₂ (1Bu⁺) state. The Raman band observed at about 1550 cm⁻¹ is assignable to the in-phase C=C stretching mode in the S₂ (1Bu⁺) state. The corresponding C=C stretching band in the S₀ (1Ag⁻) state is observed at about 1520 cm⁻¹ and that in the S₁ (2Ag⁻) state at about 1780 cm⁻¹ [2]. The changes in the C=C stretching frequencies among the three electronic states (S₀, S₁, and S₂) can be
interpreted in terms of the vibronic coupling [3] between the $S_0$ (1Ag) and $S_1$ (2Ag) states, $S_2$ (1Bu$^+$), $S_2'$ (1Bu$^-$) [4], and $S_3$ (2Bu$^-$) [5] states.

In Figure 2, the frequencies of the C=C stretching mode in the $S_2$ (1Bu$^+$) state are plotted as a function of absorption maximum (1/$\lambda_{\text{max}}$), together with the C=C stretching frequencies in the $S_0$ (1Ag) and $S_1$ (2Ag) states [2]. The value of $\nu_{\text{C=C}}$ in $S_0$ is not affected greatly by solvent [2]. In contrast, $\nu_{\text{C=C}}$ in $S_1$ [2] and $\nu_{\text{C=C}}$ in $S_2$ are significantly affected by solvent and show correlations with the absorption maxima. As 1/$\lambda_{\text{max}}$ increases (i.e., the $S_2$–$S_0$ energy gap increases), $\nu_{\text{C=C}}$ in $S_1$ increases, while $\nu_{\text{C=C}}$ in $S_2$ decreases. The observed solvent effect on the in-phase C=C stretching mode in the $S_2$ (1Bu$^+$) state is attributed to the vibronic coupling between the above five electronic states ($S_0$, $S_1$, $S_2$, $S_2'$, and $S_3$), on the assumption that the $C_{2h}$ symmetry of β–carotene is slightly broken.

References: