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Temperature induced changes in resonance Raman spectra intensity of all-*trans*-β-carotene: Changes in the fundamental, combination and overtone modes

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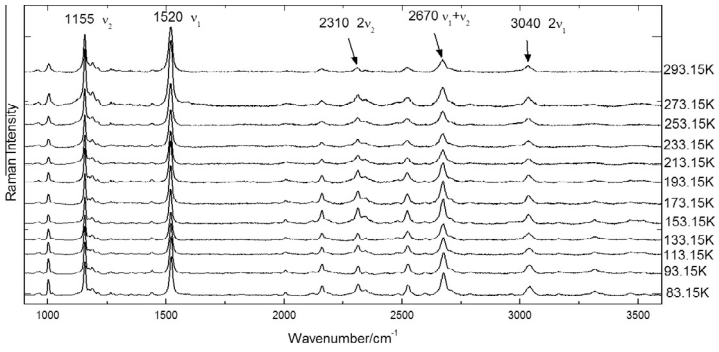
HIGHLIGHTS

- The Raman spectra of all-*trans*-β-carotene from 293 K to 83 K are obtained.
- Abnormal changes during phase transitions.
- The relative Raman intensities changes with the evolution of temperature.

GRAPHICAL ABSTRACT



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ABSTRACT

The resonance Raman spectra of the fundamental, combination and overtone modes around the C—C and C=C stretches of all-*trans*-β-carotene in 1,2-dichloroethane solution are obtained from the 293 K to 83 K temperature range. The results indicate that the intensity of the fundamentals in the liquid and solid phases generally increases as the temperature decreases, except for the liquid–solid phase transition, which exhibits a decreasing trend. The Raman intensities ratio between the fundamentals υ_1 and υ_2, combinations (overtones) and the fundamentals both increases with decreasing temperature. The Raman bandwidths of the C=C bonds gradually become narrow as the temperature decreases. These varieties of relative intensity are analyzed using the coherent weakly damped electron–lattice vibration mode, the effective conjugation length mode as well as the theory of electron–phonon interaction in this work.

Introduction

The β-carotene, with 11 conjugated double bonds in the molecule, is a non-polar carotenoid and it has many unique biochemical properties and shows biological activity [1–4]. It is one of the most extensively studied carotenoids and has been investigated in photosynthesis, in medicine, and in many fields [5,6]. We have investigated the optical properties of short-chain polymer molecule all-*trans*-β-carotene using 514.5 nm excitation. The Raman Scattering Cross Section (RSCS) of all-*trans*-β-carotene significantly increases to 10^{-23}–10^{-20} mol^{-1} Sr^{-1}, which is 10 orders of magnitude larger than that of non-polyene molecules [7–10]. The large Raman scattering cross section by the resonant Raman effects and the molecule structure order [11]. According to the nonlinear

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model, the partial CC vibrations form a coherent mode in the highly ordered all-*trans*-β-carotene chain because of extended π-electron delocalization. We associate the high Raman activity in all-*trans*-β-carotene with the collective CC vibrations generated by the π-conjugated electron. Numerous studies have been carried out to characterize the physical properties of polyene such as the coherent weakly damped CC stretching vibrations mode [11], effective conjugation length mode [12–14] and amplitude mode [15–18]. The information of all-*trans*-β-carotene under external field is so limited. We have studied the temperature effect on the combination, overtone and the fundamental modes all-*trans*-β-carotene dissolved in 1,2-dichlorothane. We give detailed theoretical knowledge on the various experimental results involved.

Experiment

All-*trans*-β-carotene was purchased from Sigma–Aldrich Chimie and stored at 255 K in the dark, and without further purified before measurement. 1,2-Dichloroethane and cyclohexane were analytical. A 5×10^{-5} M solution of all-*trans*-β-carotene was prepared by dissolving the substrate in a 25:1 mixture of reagent grade 1,2-dichloroethane and cyclohexane. The freshly prepared solution was used immediately to avoid degradation. The Raman spectra of all-*trans*-β-carotene were recorded using micro-Raman spectrometer (Renishaw InVia Raman microscope) equipped with a 514.5 nm Ar^+ ion laser. The excitation beam was positioned on a 5× objective lens to graze the surface of the sample. The integration time was 10 s for one measurement. Solution was injected in cell of heating system Linkam THMS600 which cooled by a flow of cold N_2 gas. The Raman spectra were measured at different temperature in a Linkam THMS600 system by Renishaw InVia Raman spectrometer. Absorption spectra were recorded using a Purkinje General TU-1901 spectrophotometer with 1 nm resolution.

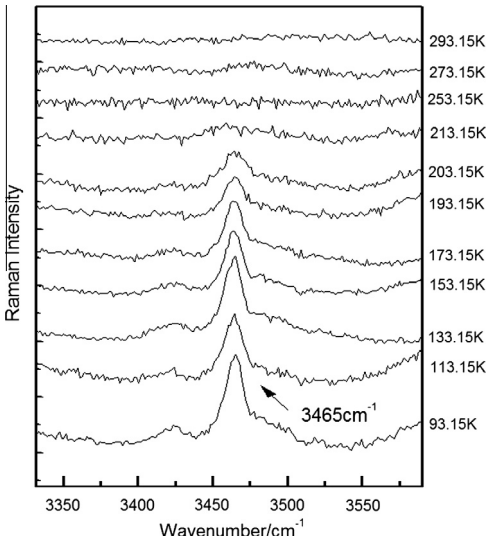

Fig. 2. The three overtone of fundamentals gradually increase with decreasing temperature the CC bond (the vertical value after enlarged twice).

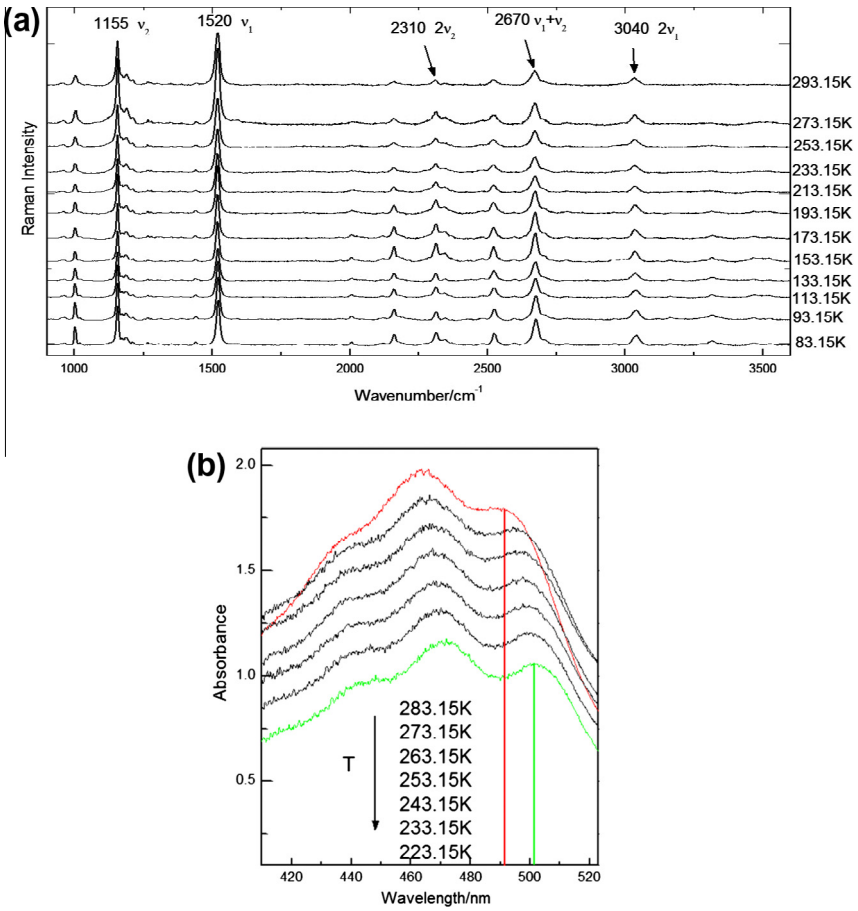

Fig. 1. (a) Resonance Raman spectra of all-*trans*-β-carotene dissolved in 1,2-dichloroethane at different temperatures (after subtraction process and baseline correction), (b) absorption spectra of all-*trans*-β-carotene dissolved in 1,2-dichloroethane at different temperatures.