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External Field Effect on Electronic and Vibrational Properties of Carotenoids

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Abstract

Resonance Raman spectroscopy is one of the most popular molecular spectroscopy methods. Using this technique, carbon-carbon (CC) vibration can be well investigated and give much information on π -conjugated system. The CC vibration has a strong dependence on the π -electron band gap, which is able to be characterized by absorption spectroscopy. Electron-phonon coupling will strongly influence the Raman intensity and shows sensitivity to the surrounding environment. Through electron-phonon coupling, CC vibration can be modulated by the π -electron band gap. In this review, we present our absorption and Raman-scattering observations of all-trans-beta-carotene from different environment such as temperature, pressure, solvents, and phase transition. The relationship between π -electron band gap and CC vibration is studied. With the decreasing of the π -electron energy, the modulation on CC vibration and electron-phonon coupling is enhanced leading to spectral red-shift. This review has significant importance in understanding the resonance Raman scattering, structural properties of polyenes, and the physics behind it. The results are also valuable for the development of fine-quality photoelectric device.

Keywords: carotenoids, absorption shift, Raman scattering cross section, electron-phonon coupling

1. Introduction

Carotenoid pigments are found in organisms from many phyla and in all wild-type photosynthetic bacteria, algae, and higher plants examined to date [1, 2]. They are important components of biomimetic photosynthetic constructs where much of the photophysics and

photochemistry including energy transfer, electron transfer, radical pair recombination observed in natural photosynthetic reaction centers, and antennas can be mimicked [2, 3]. They also have a protective function against the drastic change of the environment, that is, the dissipation of excess energy. Molecular properties of carotenoids are sufficiently studied using multiple methods. Understanding the intermolecular interactions is one of the primary objectives. Correlating the intermolecular interactions with physical properties in a condensed phase will help in interpreting the structure dependence of carotenoids in different environments [3, 4]. The all-trans- β -carotene (β -Car), with 11 conjugated double bonds, has unique biochemical and optical properties and is considered to be a model in studying conjugated polyenes. Conjugated polyenes are electroluminescent materials that are well studied because of their significance in both physics and chemistry [5–9]. This fact, combined with their functional properties of semiconductor and their solubility in common organic solvent, makes the conjugated polyenes a new class of electronic plastic materials with potential applications in electro-optical and photovoltaic devices. Many organic thin films have been fabricated and their physical properties have been examined in order to develop fine nonlinear optical devices. Carotenoids, although due to their poor structural stability, can be a good model to investigate because of their large nonlinear optical susceptibilities [9–12]. Different types of β -Car thin-films were fabricated, and their optical absorption and resonance Raman spectroscopy were examined. Photoinduced and time-resolved absorption spectroscopy reveal that the infrared absorption bands may correspond to the recombination of the soliton-like excitations in β -Car single crystals [13–16]. Spectroscopic properties and dynamics of the excited singlet states have been investigated in different liquids or polymers as a function of refractive index [17], static permittivity [18], temperature [19], pressure [20], and external electric field [21–23]. Although the solvated carotenoids have been extensively studied, the temperature dependence of Raman-active modes of carotenoids remained unknown until the work by reference [24]. The results suggested that the spectral properties of CC-stretching modes are very sensitive to the temperature, which was similar to that of polyconjugated molecules. In addition, they revealed that the temperature effect and vibronic coupling together contributed to the observed Raman mode shifts. The position of ν_1 Raman band versus conjugation chain length was revealed by combining the use of electronic absorption and Raman spectroscopy [25]. Carbon disulfide and pyridine have been chosen as solvent because of their polarizability, which are close to that of membrane lipids and proteins [26]. Observations based on different laser excitation of β -Car provided strong evidence that the enhancement of the Raman bands should be explained by electron-phonon coupling mechanism [27]. Another model, named coherent weak-damping CC vibration model, also indicated that the unusual strong intensity enhancement of polyene's overtone bands should be contributed by π -electron-phonon coupling [28]. Recent resonance Raman spectroscopic study *in vivo* concluded that the use of a high polarizability solvent was necessary to mimic the electrostatic environment *in vivo*. However, more experiments are needed on excited-state and ground-state dynamics dependence on environmental effect. Therefore, the external effects on electronic absorption and Raman scattering should be investigated and electron-phonon coupling strength in different external fields should also be examined. In this review, temperature, pressure, solvent polarizability, and phase transition effect on CC vibration modes and electron-phonon coupling are studied. The results reveal that the electron-phonon coupling can be deduced by

using the electronic band gap and Raman intensity. Different mechanisms are introduced to explain the external field dependence on β -Car electronic and vibrational properties.

2. Electronic and vibrational properties of carotenoids

β -Car has nine CC double bonds (C=C) and single bonds (C–C) and is a typical model of π -electron system. The work in early 1970s by references [29, 30] proposed that the lowest-lying excited state $S_1(2^1A_g^-)$ was silent in absorption spectrum. The most likely reason is that the Franck-Condon factors for a vertical transition are negligible since the final state is massively displaced [31]. The strong absorption of β -Car happened from π - π^* transition, which is also called $S_0(1^1A_g^-)$ - $S_2(2^1B_u^+)$ transition. The excited S_2 state decays by internal transition to S_1 , and itself decays to ground state S_0 in the same way. Recently, other “dark” states S^* have been proposed for relaxation pathways in several computational chemistry [32]. The S_0 - S_2 transition displays a characteristic three peak structure by promoting a single electron from its ground state to the lowest allowed excited state which are termed 0–0, 0–1, and 0–2 (**Figure 1**). Resonance Raman scattering is ideally vibrational technique for observation on carotenoids electronic ground state. Four main bands are observed in resonance Raman spectrum. **Figure 2** shows the resonance Raman spectrum from β -Car, four main fundamental bands are labeled from ν_1 to ν_4 . The most intense band is ν_1 from C=C vibration, which depends strongly on π -electron conjugation and molecular configuration. The ν_2 bands arise from C–C bands stretching coupled with C–H in-plane bending modes [34]. The ν_3 band around 1000 cm^{-1} is assigned as in-plane rocking vibrations of the methyl groups and ν_4 band near 960 cm^{-1} arises from C–H out-of-plane wagging motions

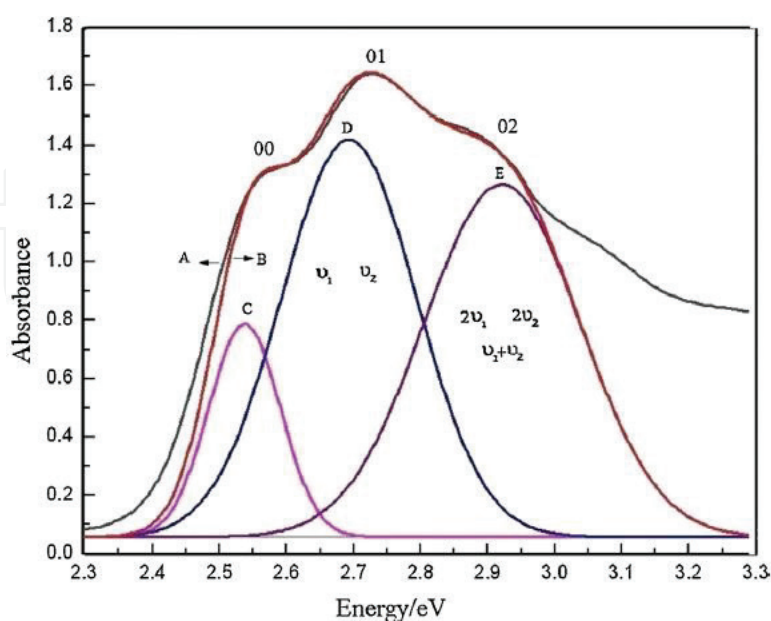


Figure 1. Absorption of β -Car dissolved in cyclohexanol. Line a represents the experimental curve and B is the fitting curve. Components C, D, and E are Gaussian deconvolution of the experimental curve (see Ref. [35]).

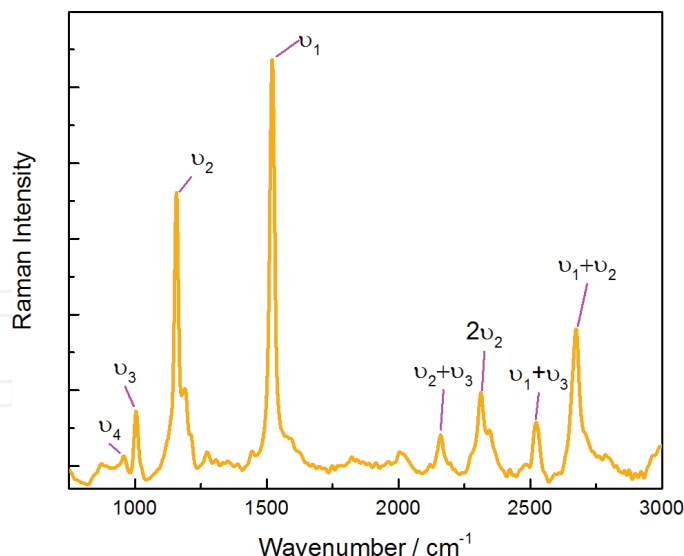


Figure 2. Raman spectrum of β -Car dissolved in carbon disulfide recorded at the room temperature. The fluorescence background has been subtracted.

coupled with C=C torsional modes. The overtone $2\nu_1$ (2310 cm^{-1}), $2\nu_2$ (3040 cm^{-1}), and combination $\nu_1 + \nu_2$ (2675 cm^{-1}) are also appeared in the resonance Raman spectrum.

3. External fields effect on electronic and vibrational spectroscopic properties

3.1. Temperature dependence on the optical properties of β -Car

There are many researches on electronic and vibrational properties on polyene. Even though the main goal of the extensive studies on polyene properties is to develop optic-electronic devices working in room temperature, studies focusing on temperature dependence of photophysical properties can provide valuable information about the electronic and vibrational characters of conjugated polyene materials. It is essential to have a profound knowledge on excited and ground states of β -Car in order to understand the mechanism of the photoprotective and antioxidative function of carotenoids. It is known that the steady-state absorption and photoluminescence spectra of inorganic materials usually red-shift with the increasing temperature [33, 35]. Extensive temperature dependence researches on conjugated polymers can provide valuable information for studying the β -Car optical response in low temperature. The spectral shift of conjugated polymers can attribute to the thermal conformational changes, which is mainly due to the change of their effective conjugation length. Using the relationship between the zero-phonon and vibrational peak intensities, we can obtain the Huang-Rhys factor. This is an effective parameter which can describe the electron-phonon coupling of the polymer material in different temperature. Given that the unexpectedly high Raman scattering activity of CC bond length vibrations is due to the extended π -conjugation giving a strong electron-phonon coupling, the π -electron delocalization and the electron-phonon coupling should show dependence on temperature.

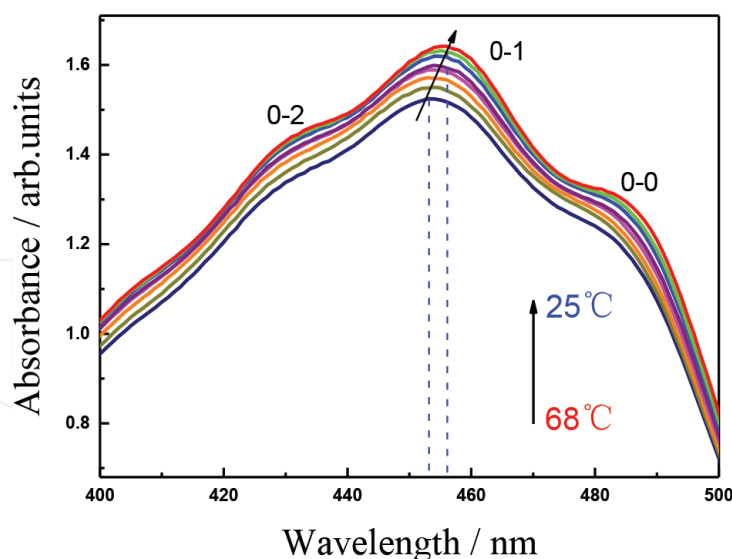


Figure 3. Absorption spectra of β -Car dissolved in cyclohexanol in different temperatures from 68 to 25°C.

We measured the absorption of β -Car dissolved in cyclohexanol in the temperature range from 68 to 25°C with an interval of 5°C. As shown in **Figure 3**, with the decreasing of the temperature, the thermal motion, the entropy of the molecule decreases and the thermal disorder of the β -Car molecule decreases. At the same time, the degree of order of the molecular structure increases, the molecule becomes straight, so that the π electron delocalization expands. The π - π^* transition energy narrows which leads to the observed absorption red-shift, which is different from the absorption properties of inorganic materials. With the narrowing of the π - π^* gap, the influence on the CC vibrational bands from electronic transition becomes stronger. Correspondingly, we recorded the resonance Raman spectra in the same temperature range in order to examine the influence from the narrowing π - π^* gap. **Figure 4** shows the resonance Raman spectra of β -Car molecule dissolved in the cyclohexanol in different temperature from 60 to 20°C with the 514.5-nm laser excitation. The bands' frequency

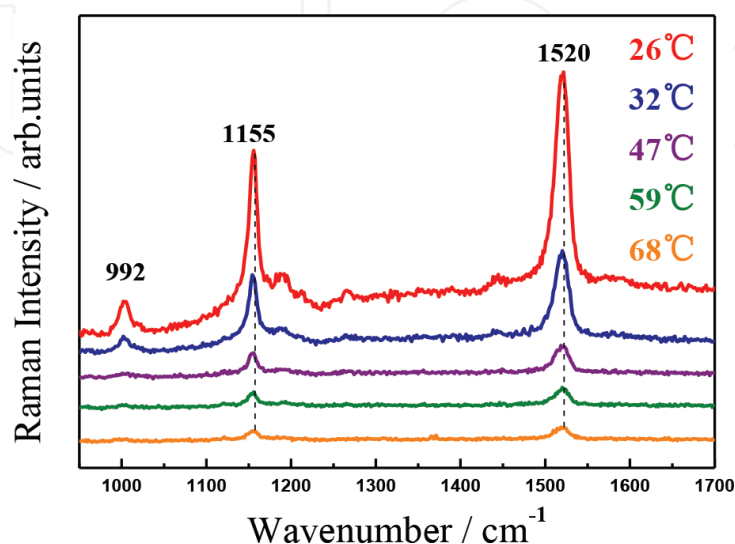


Figure 4. Resonance Raman spectra from 68 to 26°C of β -Car dissolved in cyclohexanol. The laser excitation wavelength is 514.5 nm.

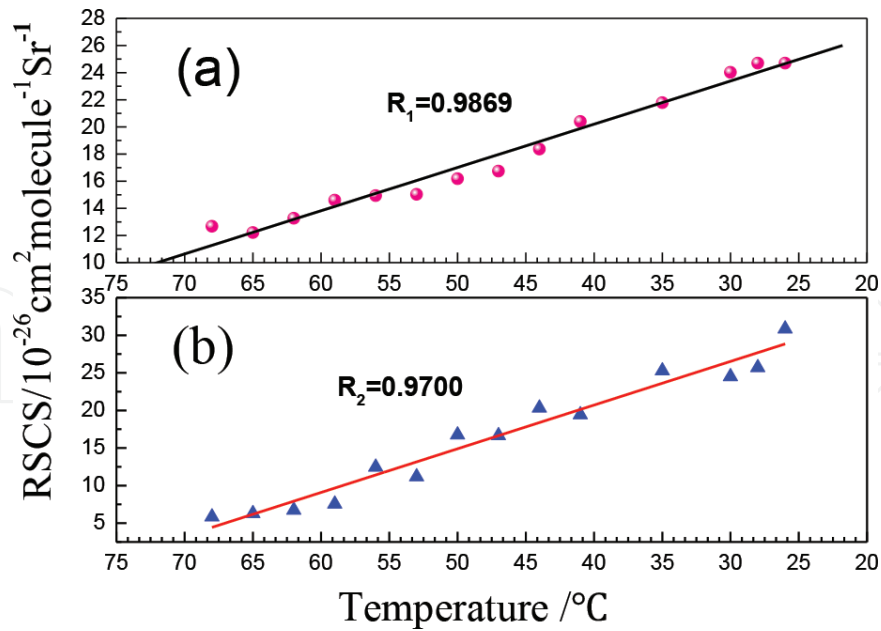


Figure 5. Temperature dependence of RSCSs from (a) C–C and (b) C=C vibrations.

present little shift in this small temperature range, which is consistent with the work by [24]. However, the intensity variation from the resonance Raman scattering results is relatively large and more obvious. Taking the advantage of the Dudik equation, we can calculate the C=C and C—C modes Raman scattering cross section (RSCS). From **Figure 5**, with decreasing temperature, the RSCS declines, which means that the π electron modulation on CC vibration is strengthened. Finally, the observed Raman intensity enhances.

In order to get an evaluation on electron-phonon coupling strength, we use the method reported by [36] to calculate the electron-phonon coupling constants and their temperature dependence which can also reflect the effective conjugation length. The equations can be expressed in the simplified form as follows:

$$S = \frac{I_{10}}{I_{00}}, \tag{1}$$

$$S = \frac{V_1^2}{\omega_1^2} + \frac{V_2^2}{\omega_2^2}, \tag{2}$$

$$\frac{I_1}{I_2} = \frac{\left(\frac{V_1^2}{\omega_1^2}\right)}{\left(\frac{V_2^2}{\omega_2^2}\right)}, \tag{3}$$

where S is the Huang-Rhys factor, I_{10} and I_{00} can be extracted from absorption spectrum, which, respectively, represents the zero-phonon line intensity and the first vibrational peak intensity. The V_1 and V_2 are the electron-phonon coupling constants, which lead to the broadening of absorption band and resonant enhancing of the two totally symmetric phonons observed in Raman scattering

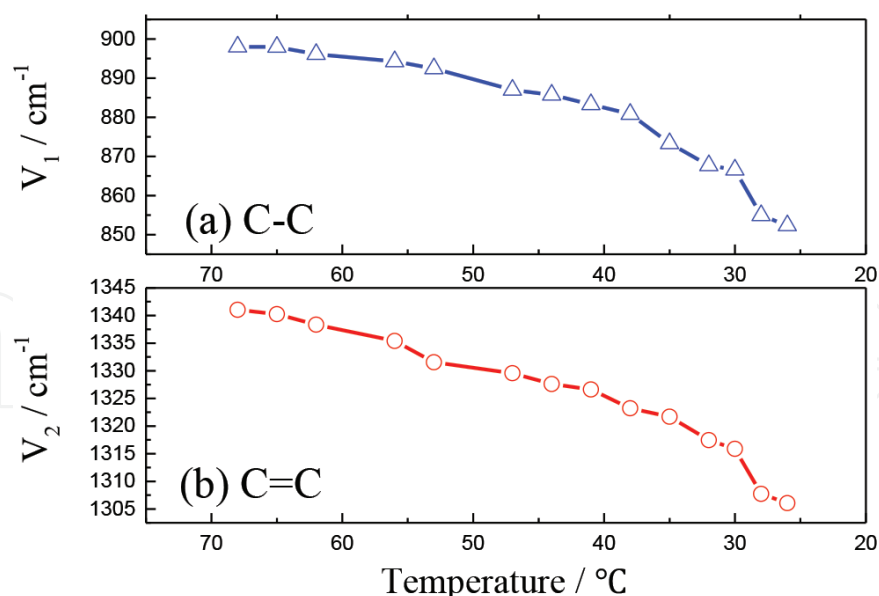


Figure 6. Temperature dependence on (a) C—C and (b) C=C electron-phonon coupling coefficient.

($\omega_1 = 1155 \text{ cm}^{-1}$, $\omega_2 = 1520 \text{ cm}^{-1}$). With the I_1 , I_2 and ω_1 , ω_2 obtained by Raman spectra, the V_1 / V_2 could be calculated. Combining this result with the value of HR factor from absorption spectrum, it is then allowed to derive the electron-phonon coupling constant for the dissolved β -Car molecule.

The results are shown in **Figure 6**, which indicate that the modulation on CC modes becomes stronger and the electron-phonon coupling is enhanced. As a result, the CC modes show Raman intensity enhancement.

3.2. Pressure dependence on the optical properties of β -Car

Pressure dependence of absorption and resonance Raman scattering of β -Car was pioneered by [37] in the 1980s. Their research firstly showed that the absorption from β -Car under pressure presented a large red-shift and a strong broadening of the vibronic peaks. This work suggested that the assumption of linear coupling of pressure to configurational coordinate needed to be modified and the potential energy curves showed pressure-induced shift. Better information about this was reported later by their works on resonance Raman scattering of β -Car. However, they concluded that the configurational coordinate models and solvent models could not sufficiently explain the large shift in the electronic spectrum of β -Car under pressure [38]. The work by Ref. [39] studied the solvent effect and pressure effect on β -Car dissolved in n-hexane and carbon disulfide. It was concluded that the spectral response from β -Car should due to the environmental effect rather than structural distortion and considered high-pressure technology as a potential way in exploring the biological functions of carotenoids.

The absorption and resonance Raman spectra of β -Car molecules at pressures of 0.04–0.60 GPa in carbon disulfide were measured. The experimental result (**Figure 7**) is that as the pressure increases, the absorption spectrum red-shifts and the reason should be the fact that the molecules are compressed and the π -electron energy gap decreases under pressure. The CC bond length is shortened, and the π -electron delocalization is blocked and thus the energy increases.

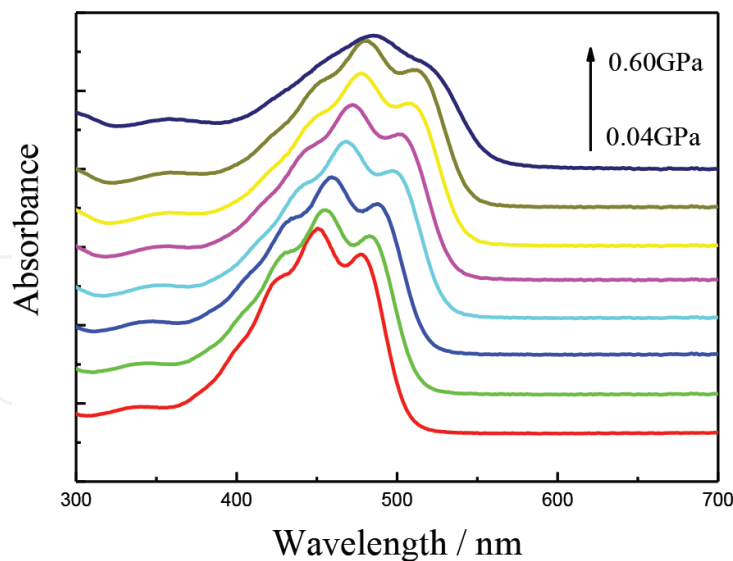


Figure 7. Absorption spectra from β -Car dissolved in carbon disulfide under pressure from 0.04 to 0.60 GPa.

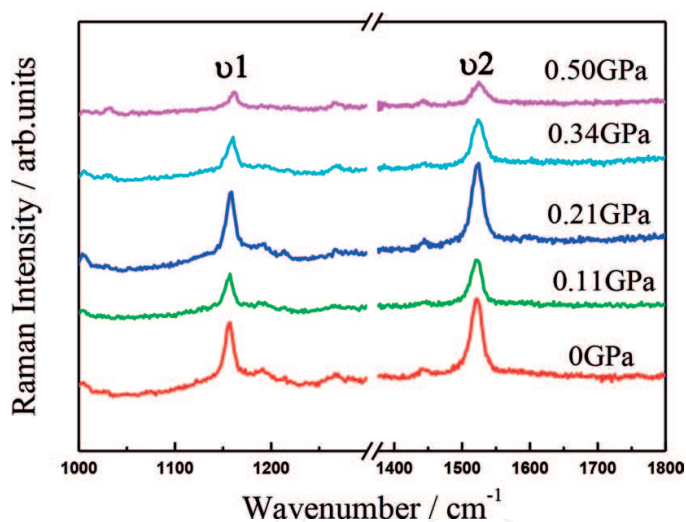


Figure 8. Raman spectra of C—C (1155 cm^{-1}) and C=C (1520 cm^{-1}) bond in different pressures.

It is evident from **Figure 8** that as the pressure increases, the Raman spectra blue-shift and the intensity of the Raman spectra decreases with increasing pressure. Obviously, the absorption spectra and Raman spectra changes are different very much from the effects of temperature on β -Car molecules. When the temperature is lowered, the absorption spectrum and the Raman spectrum are red-shifted, and the spectral intensity is increased. This is due to the π -electron energy gap that enhances the modulation of the CC bond vibration. Electron-phonon coupling enhancement is perfectly explained by theories such as “effective conjugate length” and “coherent weakly damped vibration” of linear polyene molecules. When under pressure, the absorption spectrum of β -Car is red-shifted, the Raman spectrum is blue-shifted, and the Raman intensity is reduced. The above theory cannot be explained satisfactorily. The

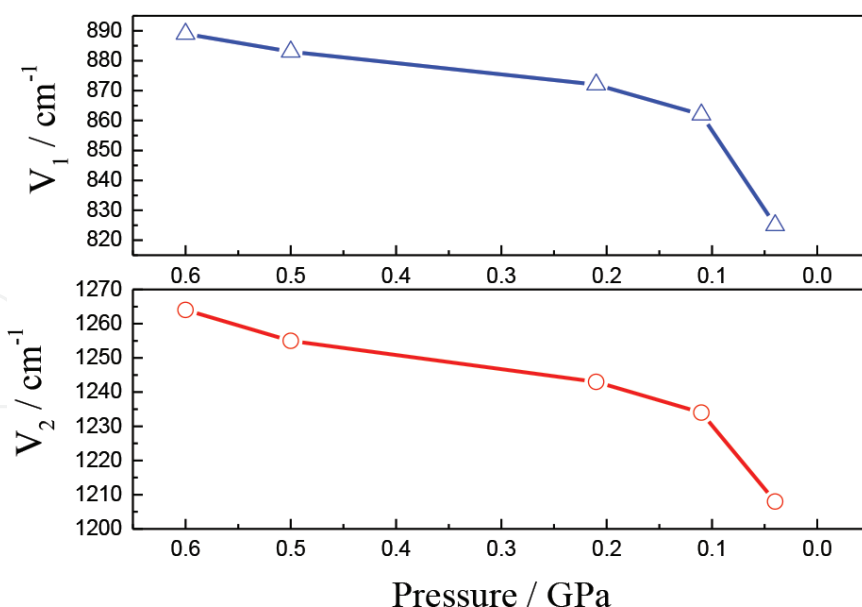


Figure 9. Pressure dependence on electron-phonon coupling coefficient V_1 and V_2 .

formation of the resonant Raman spectrum based on the linear polyene molecule is the result of the vibrational modulation process of the π -electron energy gap on the CC atom, which is the result of electron-phonon coupling. Similarly, according to **Figures 7 and 8**, using theory reported by [36], it is calculated that as the pressure increases, the electron-phonon coupling coefficient increases (**Figure 9**), that is, the electron-phonon coupling strength decreases. The π -electron energy gap weakens the modulation of the CC bond vibration. It is thus able to conclude that as the pressure increases, the β -Car molecule is compressed, the energy of the system increases, and the π -electron energy gap decreases. Therefore, the π -electron modulates the CC vibration, the Raman spectrum blue-shifts, and the intensity decreases.

3.3. Solvent effect on the optical properties of β -Car

The polarizability, polarity, density, and dielectric constant of the solvent will affect the system energy and energy gap of the π electron and thus influence the π -electron energy gap modulation on CC vibration [40]. The absorption spectra and resonance Raman spectra of β -Car in 10 different polarizability solvents were measured. As the polarizability increases, the absorption spectra of β -Car red-shifts (**Figure 10**).

This is because when the β -Car molecule is in the vibrational ground state, two π electrons in C=C are in the π bond orbital, and there is no polarity. When the π - π^* transition occurs, π electrons are in the π -bonded orbitals and the π^* anti-bond orbits, respectively, and lead to generate polarities. The excited state polarity is stronger, so that the energy drop is greater than the ground-state energy. Therefore, the difference between the π electron energies becomes smaller. At the same time, as the polarizability increases, the concentration of the solution density increases, the space of the β -Car molecule swing decreases, and the order of the molecular structure increases. In this context, the effective conjugate length increases.

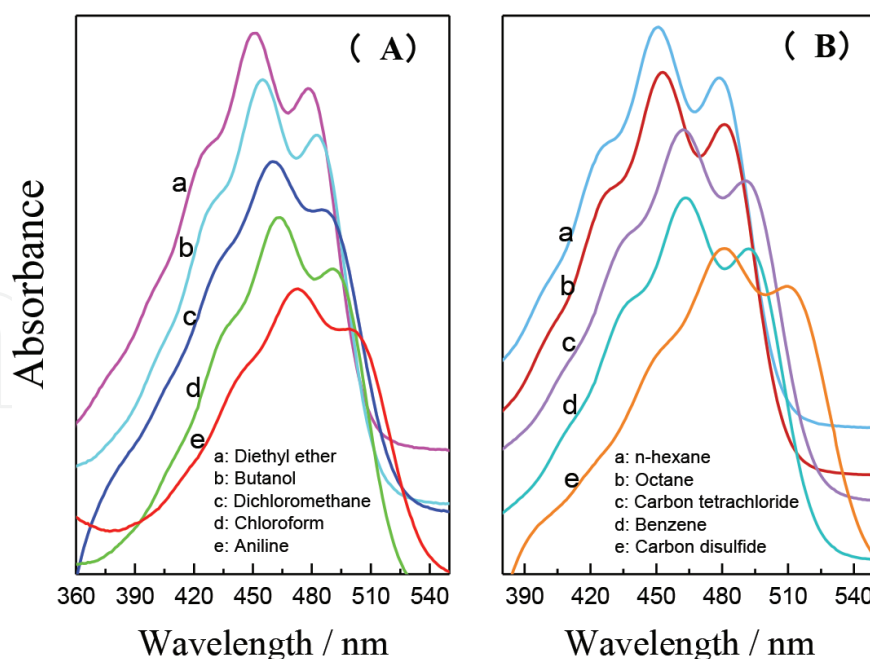


Figure 10. Absorption spectra of β -Car in (a) polar solvents and (B) non-polar solvents.

The reduction of the π -electron energy gap causes red-shift of the electron absorption peak. **Figure 11** shows the resonant Raman spectra of measured C—C, C=C modes of β -Car molecules. Extracting data from **Figure 11**, it can be calculated that as the solvent polarizability increases, the Raman scattering cross section of the CC bond increases. The increase in the polarizability and the increase in the molecule induced dipole moment.

According to **Figures 10** and **11**, using the method of calculating electron-phonon coupling constant by [36], the variation law of electron-phonon coupling coefficient with solvent polarizability is obtained (**Figure 12**). It is able to conclude that as the polarizability increases, the π -electron energy gap enhances the modulation of the CC bond vibration, the electron-phonon coupling coefficient decreases, the electron-phonon coupling increases, the Raman activity increases, and the Raman cross section increases. It is clear that as the solvent polarizability increases, the π -electron energy gap increases the modulation of the CC bond vibration.

3.4. Phase transition on the optical properties of β -Car

Investigation on β -Car solution in different phases should give more information on its electronic and vibrational states. Physical properties of carotenoids in a condensed phase were pioneered by Hashimoto et al., whose study included a wide range of researches on different types of films and their optical properties. Not surprisingly, their work provides valuable information on electronic and vibrational dynamics of optically forbidden $2^1A_g-A_g$ transition. Their observation of soliton-like excitations gave a new method in studying the physical properties of carotenoids and related their optical properties to the one-dimensional conducting polymers. The physical properties of β -Car in solid phase and liquid phase are quite different due to the polyene structure and the solvent effect. These two effects jointly lead to variation on optical response when the solution is in different phases.

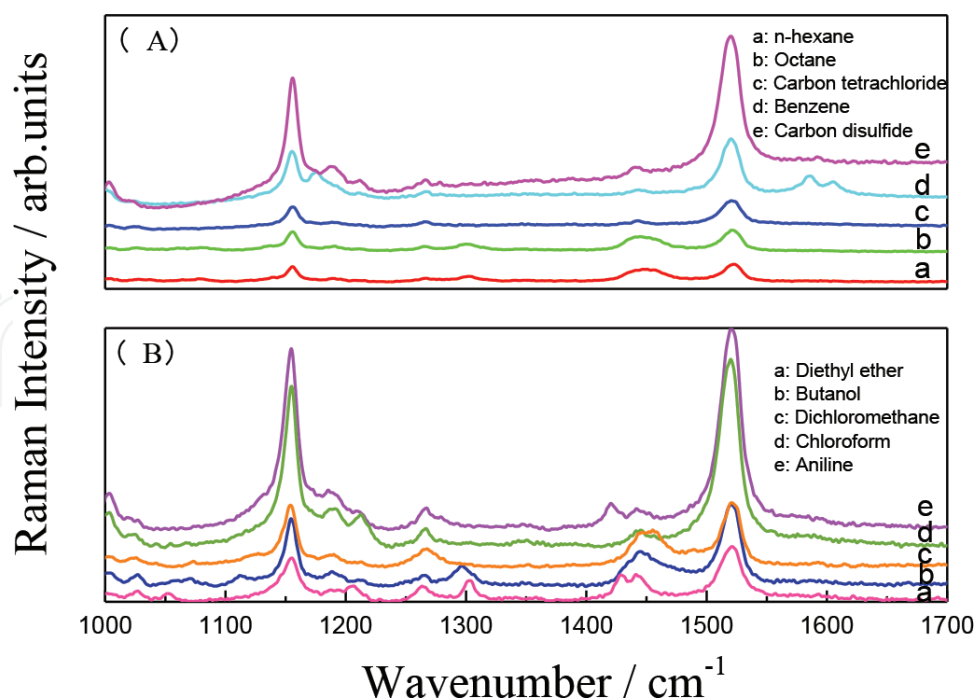


Figure 11. Raman spectra of β -Car in (a) non-polar solvents and (B) polar solvents.

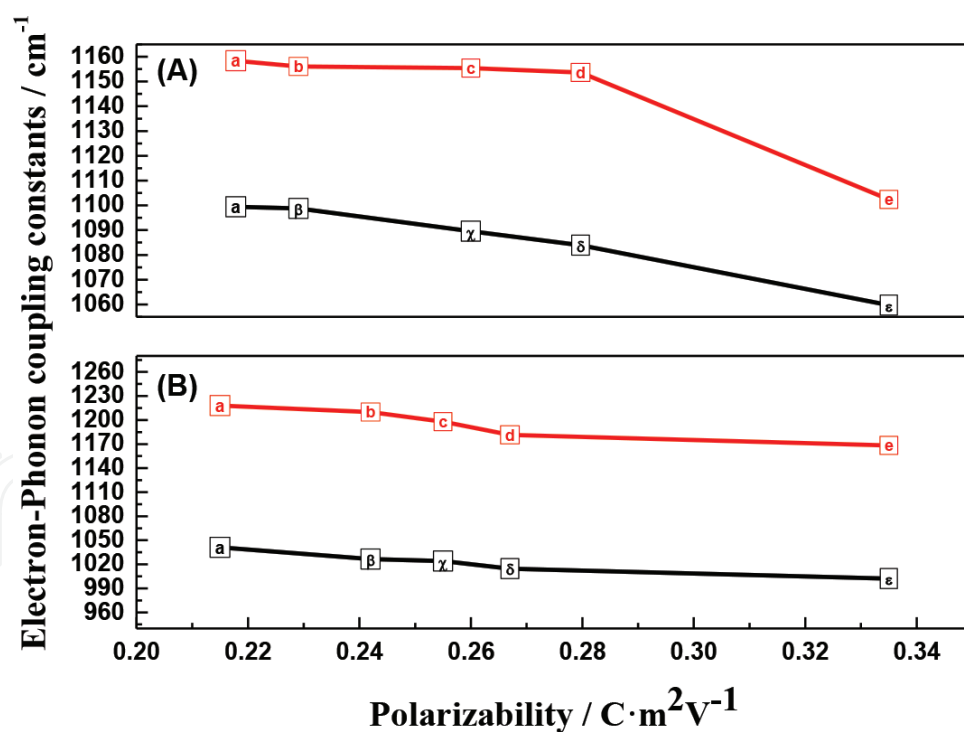


Figure 12. The relationship between electron-phonon coupling coefficient and polarizability in (a) non-polar and (b) polar solvents.

Figures 13 and 14 show the absorption and resonance Raman spectra of β -Car dissolved in cyclohexanol at 65–22°C. As the temperature decreases, the solution undergoes liquid-solid phase change at 20°C. From Figure 13, we can find that with a decreasing temperature, the

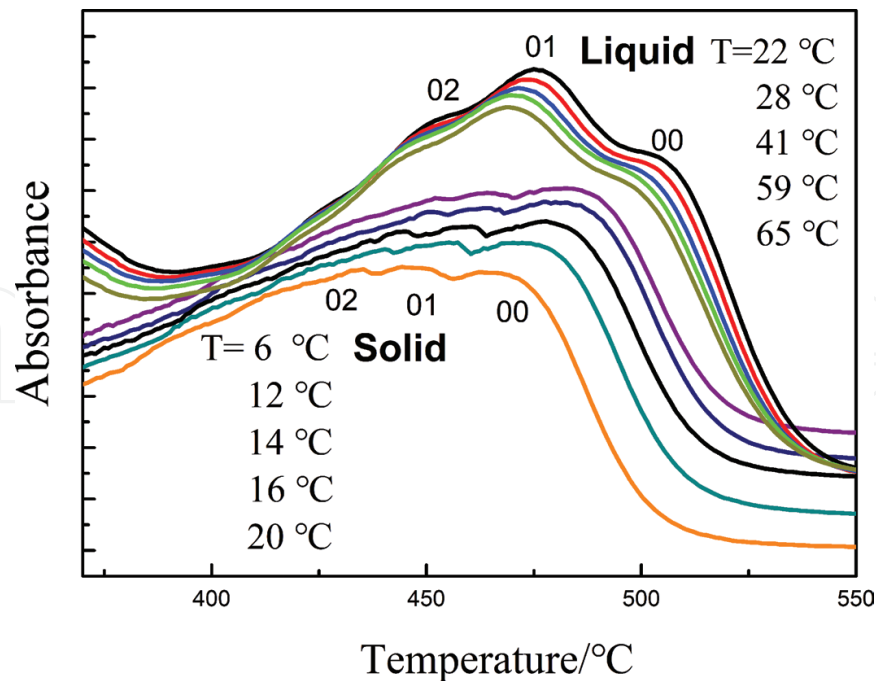


Figure 13. Absorption spectra of β -Car dissolved in cyclohexanol in different temperatures.

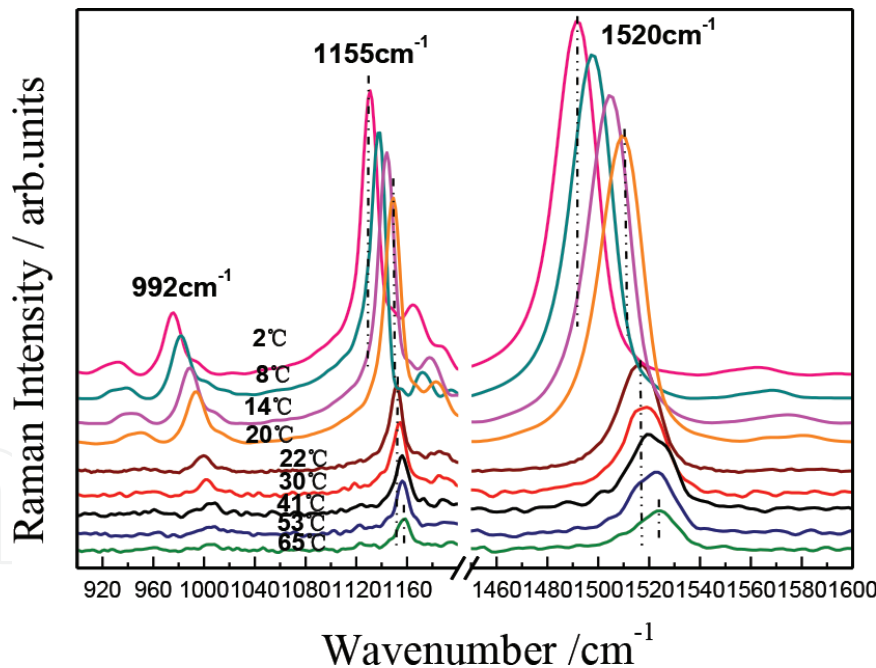


Figure 14. Raman spectra of C—C and C=C vibration of β -Car dissolved in cyclohexanol in different temperatures.

absorption spectra of β -Car molecules red-shift when the solution is in both liquid and solid phases. The solid phase ($R = 2.24 \text{ nm/}^\circ\text{C}$) absorption spectral red-shift is greater than that of liquid phase ($R = 0.23 \text{ nm/}^\circ\text{C}$). This result shows that the electron-phonon coupling of β -Car in solid phase has a more sensitive temperature dependence compared to the liquid phase. From **Figure 14**, the resonance Raman spectra show a similar changing tendency upon temperature.

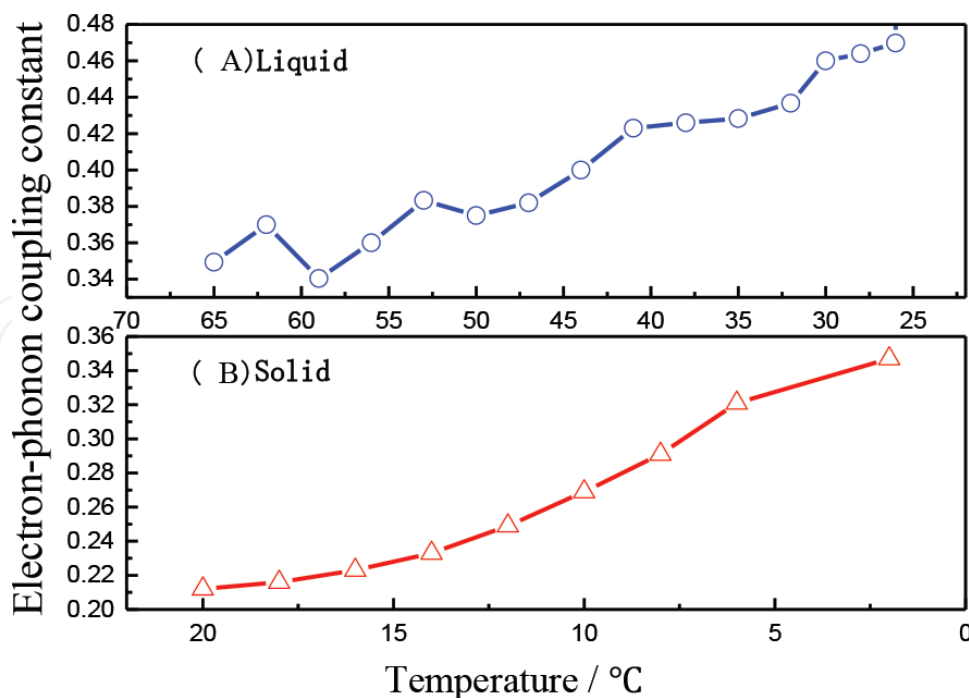


Figure 15. Temperature dependence of β -Car molecular electron-phonon coupling coefficient λ (A) before and (B) after phase transition.

With the decrease of temperature, the CC modes red-shift and their intensity enhance. The shift magnitude becomes larger after the solution phase transition, which is consistent with the absorption results. In the solid phase, there is no Brownian motion, the molecular density increases, and the movement of the β -Car molecule is prevented. Increasing the molecular structure of β -Car in an orderly manner reduces the energy of the system, the π -electron energy gap is greatly affected by temperature, the modulation of CC bond vibration is enhanced, the coupling of electron-phonon is enhanced, and the Raman-active mode red-shift is accelerated. The spectral intensity increases. According to the relationship between energy gap E_g and the coupling coefficient $E_g \sim \exp(1/2\lambda)$, as well as λ and $\omega_1, \omega_2, 2\lambda \sim (\omega_1 \omega_2 \omega_3)^2$, the relationship between temperature and coupling coefficient can be calculated [41]. **Figure 15** shows the relationship between the electron-phonon coupling coefficient and the temperature before and after the phase change.

4. Conclusion

Resonance Raman spectroscopy is one of the main spectral technologies for the study of linear polyene molecules. Raman spectroscopy is the result of π -electron energy gap modulation of CC atoms. External fields such as temperature, pressure, solvent effect, and phase transition have influence on the degree of ordering of polyene molecules, the effective conjugate length, and the degree of electron delocalization, and the physics behind the phenomenon of the influence by different external fields on these characteristics are not the same. Changing the system energy, the absorption spectrum would show a red-shift or a blue-shift, and the

corresponding electron-phonon coupling increases or decreases. Finally, different modulation modes are generated for the C–C and C=C vibration. In general, when the system energy decreases, the π electron energy gap is reduced. With a decreasing energy gap, the modulation is enhanced, and the electron-phonon coupling is strengthened. Raman spectra will red-shift and their intensity is enhanced and vice versa.

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Conflict of interest

The authors declare no conflict of interest.

Thanks

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