Difference in effect of temperature on absorption and Raman spectra between *all-trans-β*-carotene and *all-trans-retinol**

Qu Guan-Nan(曲冠男)[a)b)], Li Shuo(李 硕)[a)], Sun Cheng-Lin(孙成林)[a)], Liu Tian-Yuan(刘天元)[a)], Wu Yong-Ling(吴咏玲)[a)], Sun Shang(孙 尚)[a)], Shan Xiao-Ning(单肖宁),[a)] Men Zhi-Wei(门志伟)[a)b)†], Chen Wei(陈 伟)[c)‡], Li Zuo-Wei(里佐威)[a)], and Gao Shu-Qin(高淑琴)[a)]

[a)] *College of Physics, Jilin University, Changchun* 130012, *China*

[b)] *State Key Laboratory of Superhard Materials, College of Physics, Jilin University, Changchun* 130012, *China*

[c)] *The Third Hospital , Jinlin University, Changchun* 130021, *China*

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Temperature dependencies (81 °C–18 °C) of visible absorption and Raman spectra of *all-trans-β*-carotene and *all-trans*-retinol extremely diluted in dimethyl sulfoxide are investigated in order to clarify temperature effects on different polyenes. Their absorption spectra are identified to be redshifted with temperature decreasing. Moreover, *all-trans-β*-carotene is more sensitive to temperature due to the presence of a longer length of conjugated system. The characteristic energy responsible for the conformational changes in *all-trans-β*-carotene is smaller than that in *all-trans*-retinol. Both of the Raman scattering cross sections increase with temperature decreasing. The results are explained with electron–phonon coupling theory and coherent weakly damped electron–lattice vibrations model.

Keywords: *all-trans-β*-carotene, *all-trans*-retinol, redshift, Raman scattering cross section

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1. Introduction

Conjugated polyenes are electroluminescent materials which present high quantum efficiencies at room temperature. There is a lot of research about the polyenes.[1,2] 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.[3,4] *All-trans-β*-carotene and *all-trans*-retinol each consist of a β ionone core and a conjugated polyene chain. *All-trans-β*-carotene and *all trans*-retinol are important in many essential biological processes, including vision,[5] reproduction,[6−8] glycoprotein synthesis,[8] and cell growth.[9] The conjugated polyenes are sensitive to oxygen and light.[10−15] Even though the main goal is to develop a polymer working at room temperature, studies focusing on the temperature dependence of photophysical phenomena[16−18] can provide valuable information about the absorption and Raman characteristics of conjugated polyenes materials.

The reduction of temperature can reduce the inherent conformational disorder which often reduces the electron delocalization in these π-conjugated systems.[19] The conformational changes can be regarded as thermal excitation of certain vibrational modes into higher energy levels. We may assume a single vibrational mode with energy ε to be responsible for the conformational change for simplicity.

In this paper, temperature dependencies (81 °C–18 °C) of visible absorption and Raman spectra of *all-trans-β*-carotene and *all-trans*-retinol extremely diluted in dimethyl sulfoxide (DMSO) are investigated in order to clarify temperature effects on different conjugated length polyenes. The temperature dependence of the zero-phonon line in the absorption is

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†Corresponding author. E-mail: zwmen@jlu.edu.cn

‡Corresponding author. E-mail: chenwei1999@gmail.com

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attributed to an increase in the liquid density and the concomitant increase in the refractive index by the Lorentz–Lorenz relation at low temperature. The enhancement of coherent weakly damped electron–lattice vibrations leads to the increases of the Raman scattering cross sections (RSCSs) of *all-trans-β*-carotene and *all-trans*-retinol.

2. Experimental details

Retinoid powders (*all-trans*-retinol and *all-trans-β*-carotene) were purchased from Sigma-Aldrich Chimie (France) and stored at −20 °C in the dark. The experiment was performed on a solution of *all-trans*-retinol which was dissolved in DMSO, and *all-trans-β*-carotene dissolved in benzene and DMSO. DMSO was used as solvent, as had been done in previous papers.[20] The mixture of benzene and DMSO was well used as a solvent in variable temperature experiments. First, DMSO has a hard volatile characteristic, for it is easy to freeze when being dissolved in organic solvents at low temperature. Second, its position of Raman band is far away from that of *all-trans-β*-carotene. These factors have no influence on our processing data. Fresh solutions were measured immediately after their preparation to avoid degradation. The peculiarities in the Raman spectra that we observed at 1044 cm^{-1} of DMSO and 992 cm^{-1} of benzene can be used as interior indications for *all-trans-β*-carotene and *all-trans*-retinol. The 514.5-nm line from an Ar^+ ion laser was used as the excitation source, with a laser power of 3.6 mW. The spectra were collected in a backscattering configuration by a microscope using a 5× objective. The Raman spectra of the more intense lines were measured at different temperatures in a Linkam thms600 system and recorded on a Renishaw InVia Raman spectrometer (Spectra Physics163-M42). The absorption spectra were measured on a Purkinje General TU-1901 spectrophotometer with 1-nm step.

3. Results and discussion

3.1. Temperature evolutions of visible spectra of *all-trans-β*-carotene and *all-trans*-retinol

All-trans-β-carotene is characterized structurally by a short, conjugated, π-electron chain of 9 conjugated double bonds in its hydrocarbon backbone and spectrally by strong visible absorption in the 400 nm–500 nm region.[21,22] And *all-trans*-retinol has 4 repeat units and is characterized by strong visible absorption in the 300 nm–380 nm region.[23] The structures are given in Fig. 1. The absorption of *all-trans-β*-carotene is due to an intense, allowed $S_0(1^1A_g^-) \rightarrow S_2(1^1B_u^+)$ transition. Transition between $S_0(1^1A_g^-)$ and the lowest excited singlet state, $S_1(2^1A_g^-)$ is forbidden by symmetry.[21,24] Figure 2 shows the absorption spectra for the *all-trans-β*-carotene and *all-trans*-retinol at different temperatures.

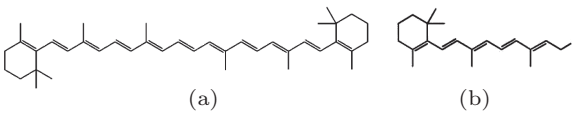


Fig. 1. Structures of *all-trans-β*-carotene (a) and *all-trans*-retinol (b).

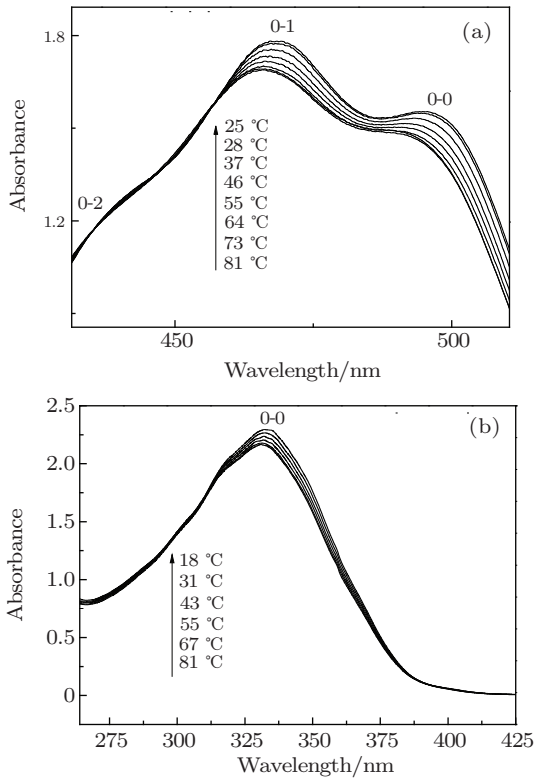


Fig. 2. Visible absorption spectra of *all-trans-β*-carotene (a) and *all-trans*-retinol (b) dissolved in DMSO in a temperature range from 81 °C to 18 °C. The zero-phonon peaks and the first and second vibronic bands are denoted as the 0-0, 0-1, and 0-2 peaks, respectively.

Figure 3 shows the temperature dependencies of the wavelength of *all-trans-β* carotene and *all-trans*-retinol in DMSO. The slopes of both bands are positive, but the former increases more rapidly than the latter.

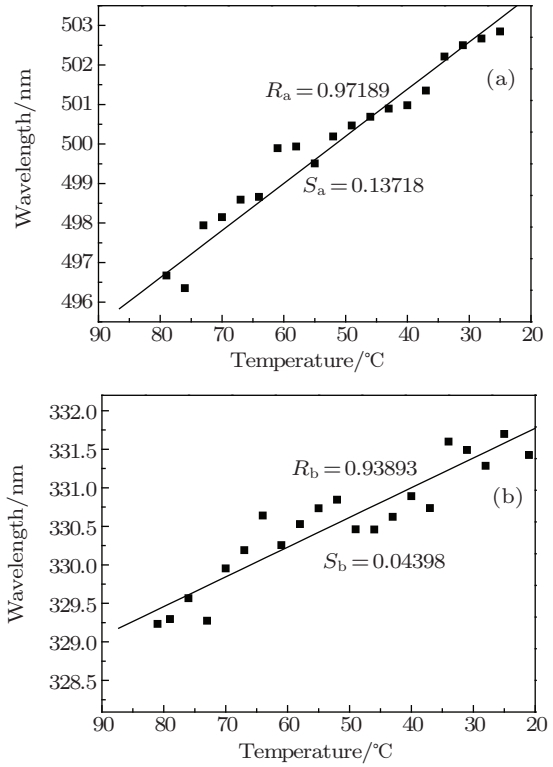


Fig. 3. Temperature dependencies of absorption electronic (0–0) transition peak wavelength of *all-trans*-β-carotene (a) and *all-trans*-retinol (b). The slopes (S) obtained from line fitting are also presented with wavelength being in nm and temperature in °C.

We have already described the changes of spectra on cooling the *all-trans*-β-carotene and *all-trans*-retinol. The measurements are summarized in Table 1. As already noted, the *all-trans*-β-carotene and *all-trans*-retinol on cooling to about 18 °C, exhibit values of displacement $\lambda_{\max}$ of about 7.68 nm and 2.81 nm of the central maximum toward longer wave-lengths, and the values of ratio $\varepsilon_{\max}$ of increasing about 6 and 5 percent. Ratio $\varepsilon_{\max}$ itself, though frequently involved in theoretical discussion, has little physical meaning, and offers only a rough hint of whether the band area has changed. As shown by the polyenes examined, the *all-trans*-β-carotene exhibits special behaviour. Cooling it shifts $\lambda_{\max}$ more than cooling *all-trans*-retinol. The major different feature of them is that they possess different conjugated systems of alternate single and double bonds in linear array.

Resonance, or the presence of π-electrons, lowers the energy required to raise an electron from the ground state to the first excited state, hence poising the absorption at relatively long wave-lengths; and also greatly increases the probability of such transitions, resulting in a consequent intensification of absorption.[23]

The peak shift of the optical spectrum, induced by a change in the refractive index, is generally described by[25,26]

$$E = E_0^0 + p\frac{n^2-1}{n^2+2}. \tag{1}$$

Here, $(n^2-1)/(n^2+2) = \phi(n^2)$ is the Lorentz–Lorenz function, and E_0^0 and p are the intercept peak energy and the slope in the plot of peak energy E against $\phi(n^2)$, respectively. In this case, the refractive index function $\phi(n^2)$ reflects the interaction of traveling light with matter[27,28] and varies with temperature. The temperature variation of $\phi(n^2)$ can be evaluated by

$$\phi(n^2) \propto \rho/M \propto l^{-3}, \tag{2}$$

where ρ and M are the density and the molecular weight of surrounding matter, respectively, and l is the length of the sample.

Table 1. Parameters of absorption spectra for *all-trans*-β-carotene and *all-trans*-retinol.

Sample	81 °C		18 °C		Ratio of $\varepsilon_{\max}$	Shift of $\lambda_{\max}$/nm
	$\varepsilon_{\max}/10^{-3}$	$\lambda_{\max}$/nm	$\varepsilon_{\max}/10^{-3}$	$\lambda_{\max}$/nm	(18 °C/81 °C)	(18 °C/81 °C)
All-trans-β-carotene	16.91	495.17	17.98	502.85	10633	7.68
All-trans-retinol	21.69	329.23	22.94	332.04	1.0576	2.81

In the temperature range studied it is found that the measurements of density and refractive index vary linearly with temperature. For $T = 60$ °C: $\rho = 1.060398$ g/cm^3 and $n = 1.4620$ while for $T = 20$ °C: $\rho = 1.100401$ g/cm^3 and $n = 1.4793$.[27] So the red shifts of the absorption spectrum of *all-trans*-β-carotene and *all-trans*-retinol in the visible region upon temperature decreasing should be explained as arising from the increase in liquid density and the concomitant increase in refractive index by the Lorentz–Lorenz relation.

Otherwise, the increase of the effective conjugation length with temperature decreasing can be described in terms of the chain conformational order

through the expression[30]

$$n(T) = n_0 \, \mathrm{e}^{\varepsilon KT}, \tag{3}$$

where n_0 is the effective conjugation length at high temperatures, k is the Boltzmann constant, and ε is the characteristic energy responsible for the conformational changes in the polymer chains.

Figure 4 shows the temperature behaviors of the 00 absorption peak energy of *all-trans*-β-carotene and *all-trans*-retinol. The fit curves (dot lines) are obtained from the empirical expression[31–33]

$$E = E_0 + \frac{\Delta}{n\,(T)}, \tag{4}$$

where E_0 is the respective gap energy in the absorption case and Δ is a fitting parameter, dependent on the polymeric material. For practical purposes we refer to Δ/n_0 as ΔE in order to simplify the fitting process. For E_0, we use the gap energy at 298 K in Fig. 4.

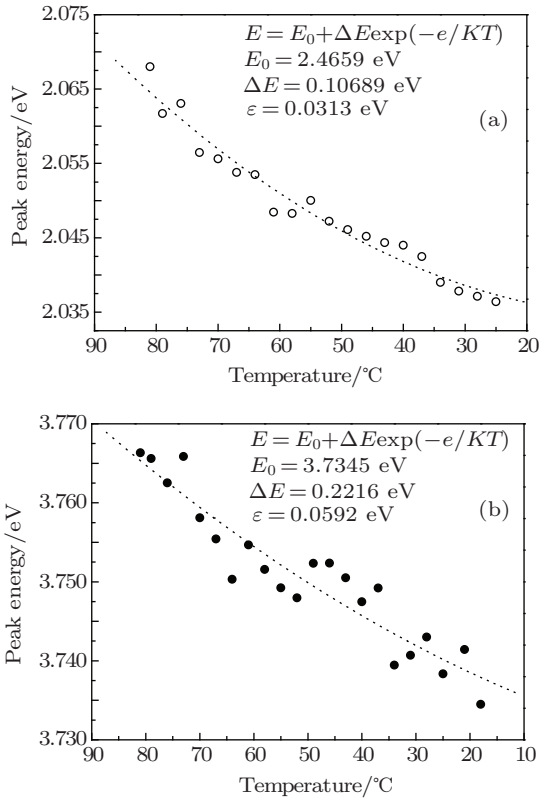


Fig. 4. Temperature dependencies of the absorption zero-phonon peak energy of *all-trans*-β-carotene (a) and *all-trans*-retinol (b). The dot lines are the curves fit to experimental data as explained in the text.

The energy ε for *all-trans*-β-carotene [ε = 0.0313 eV, Fig. 4(a)] is lower than that obtained from the fit in the *all-trans*-retinol [ε = 0.0592, Fig. 4(b)]. The energy ε represents the characteristic value of energy to change the conformation of the polymeric chain. Another parameter which is very sensitive to the electronic delocalization is the bond length alternation (BLA), i.e., the average difference between single and double C–C bond length. An increase in delocalization length implies an increasing equalization of the chain length. It is shown that there is a decrease of BLA as the chain length increases. The parameter $\bar{\lambda}$ is an a dimensional parameter introduced by Ehrenfreund *et al.*[34] to express the electron–phonon coupling in polyene chains of a given length. It is shown that $\bar{\lambda}$ decreases with the conjugation length increasing.[35] So the value of $\bar{\lambda}$ of *all-trans*-β-carotene (9 repeat units) is smaller than of *all-trans*-retinol (4 repeat units). In the *all-trans*-retinol (preponderance of small conjugation length segments) we should have a higher ε than that in the *all-trans*-β-carotene, which is in agreement with the obtained parameter.

3.2. Temperature evolutions of Raman spectra of *all-trans*-β-carotene and *all-trans*-retinol

The Raman scattering experiments demonstrate that the vibration frequencies 1520 cm^{-1} and 1590 cm^{-1} correspond to the carbon–carbon double bond stretches of *all-trans*-β-carotene and *all-trans*-retinol which contain 9 and 4 alternate double bonds respectively. In Fig. 5 the microsoft Raman spectra obtained at different temperatures are shown.

The Raman shift in the carbon–carbon double bond region behaves as a function of inverse conjugation. Since the polyenes we have examined are fully conjugated, i.e., the conjugation length is equal to the length of the molecule, we can ask what the present data suggest for the conjugation length of polyenes. The Raman shift increases with conjugation length decreasing[36]

We can obtain the RSCSs of *all-trans*-β-carotene and *all-trans*-retinol in DMSO at different temperatures using the following equations:[37,38]

$$\sigma_{\mathrm{S}} = \sigma_{\mathrm{R}} \cdot \left(\frac{I_{\mathrm{S}}}{I_{\mathrm{R}}}\right) \left[\frac{v_0\,(v_0 - v_{\mathrm{R}})^3}{v_0\,(v_0 - v_{\mathrm{S}})^3}\right] \left(\frac{C_{\mathrm{R}}}{C_{\mathrm{S}}}\right) L\,(v_0)\,, \tag{5}$$

$$L(v_0) = \left(\frac{n^2+2}{3}\right)^4, \tag{6}$$

where subscripts S and R denote solute and interior respectively; σ is the RSCS; C is the molar concentrations; I represents the Raman intensity; v_0 is the incident excitation beam wavenumber (cm^{-1}); $L(v_0)$

is the local field correction factor obtained from Onsager's theory; n is the solvent refractive index. However, $\sigma_{\rm R}$ varies with temperature. So we set the value of $\sigma_{\rm R}$ at room temperature as the label to amend the parameter. It is clear that the values of relative RSCS of all-*trans*-β-carotene and *all-trans*-retinol increase linearly with temperature decreasing (see Fig. 6).

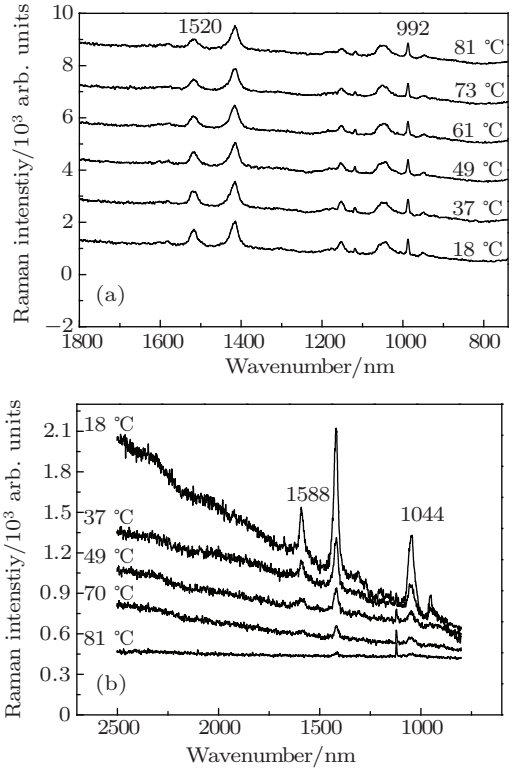


Fig. 5. Temperature dependencies of Raman spectrum of *all-trans*-β-carotene and *all-trans*-retinol dissolved in DMSO in a range from 81°C to 18 °C

The solution volume density becomes large and the intermolecular distance diminishes with the decrease of temperature. It reduces the vibrations out of the planes of the chain of *all-trans*-β-carotene and *all-trans*-retinol. At the same time, the decrease of the thermal disorder causes the electrons to stay in a low delocalization condition. This reduces the concentration of thermal defects in the chain, and the conjugated chain tends to increase the structure ordered,[39] thereby increasing the coherent weakly damped electron–lattice vibrations. The π-conjugated system is thought to be a highly sensitive superstructure which can be easily disturbed by structural defects.[40] Thus, the temperature drop increases the liquid density and the refractive index which leads to the red shifts in the absorption spectra of *all-trans*-β-carotene and *all-trans*-retinol. So the 514.5-nm excitation line can clearly drop in the absorption band of *all-trans*-β-carotene and approach the absorption band of *all-trans*-retinol, which enhances the resonant Raman effects . Therefore, the RSCS of the CC bond increases with temperature decreasing.

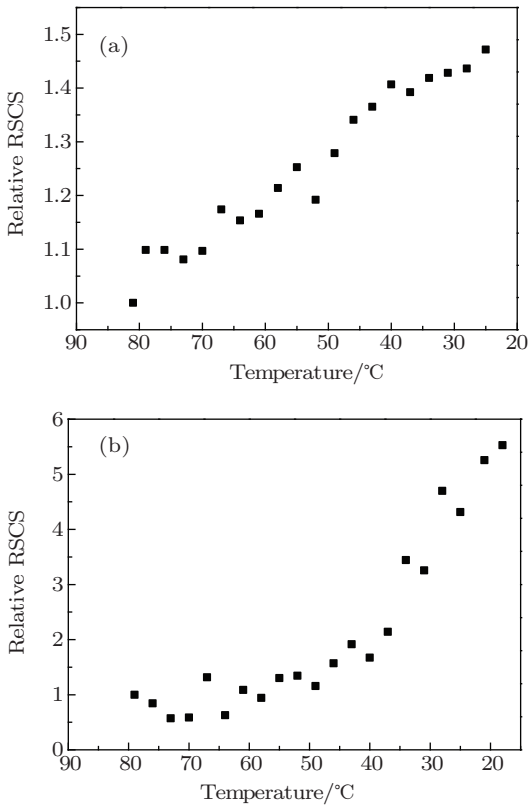


Fig. 6. Relative RSCSs of C=C of *all-trans*-β-carotene (a) and *all-trans*-retinol (b) versus temperature.

4. Conclusion

Optical absorption and Raman measurements at different temperatures are performed to characterize the optical properties of *all-trans*-β-carotene and *all-trans*-retinol. Their absorption spectra are identified to be redshifted with the decrease of temperature. The former is more sensitive to temperature because it possesses a larger conjugated system of alternate single and double bonds in linear array. An increase in chain length implies a reduction in electron–phonon coupling parameter, so it will expend lower characteristic energy on the conformational changes in the *all-trans*-β-carotene chains than in the *all-trans*-retinol chains. The enhanced coherent weakly damped electron–lattice vibrations lead to the increased RSCSs of the CC double bonds of *all-trans*-β-carotene and *all-trans*-retinol with the decrease of temperature.

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