Influence of the ordered structure of short-chain polymer molecule all-*trans*-β-carotene on Raman scattering cross section in liquid*

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We measured the resonant Raman spectra of all-*trans*-β-carotene in solvents with different densities and concentrations at different temperatures. The results demonstrated that the Raman scattering cross section (RSCS) of short-chain polymer all-*trans*-β-carotene is extremely high in liquid. Resonance and strong coherent weakly damped CC bond vibrating properties play important roles under these conditions. Coherent weakly damped CC bond vibration strength is associated with molecular ordered structure. All-*trans*-β-carotene has highly ordered structure and strong coherent weakly damped CC bond vibrating properties, which lead to large RSCS in the solvent with large density and low concentration at low temperature.

Keywords: Raman scattering cross-section, polymer molecule, ordered structure

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1. Introduction

All-*trans*-β-carotene molecule is a nonpolar carotenoid with 11 conjugated double bands which has the light collection and optical protection functions.[1] It can be applied as molecular wires and dry element cell photoconducting device.[2] All-*trans*-β-carotene is a very interesting polymers, many biologic processes and chemical reactions are conducted in liquid phase, which have eignificance in bio-molecular structure and properties.[3−6] We studied the optical properties of all-*trans*-β-carotene in liquid phase, and it is a short-chain polymer molecule that has similar properties to long-chain polymer molecules in liquid phase. Different levels of the molecular ordered structure show different properties in various liquids phase.

Raman scattering cross section (RSCS) is an important parameter, it shows the molecular microscopic properties as well as the Raman shift and the line width.[7,8] RSCS is related to temperature, solvent density and solution concentration. The RSCS is extremely large under conditions of low temperature, large density and low concentration.

We conducted the experiment on RSCS under these conditions and analysed it using the coherent weakly damped CC bond vibrating model proposed by Paraschuk.[9]

2. Experiment

The all-*trans*-β-carotene we used was the product of Sigma and stored at minus 18 degrees in the dark, and was used without further purification. All liquid reagents were analytical reagents.

The micro Raman spectrometer (Renishaw In-Via Raman microscope) is equipped with a 514.5 nm Ar^+ ion excitation laser (Spectra Physics163-M42). 5×objective (LEICA DMLM 0.12NA) is used for both laser illumination and Raman backscattering detection. Otherwise, the temperature controlled Raman spectrometer (Linkam thms600) was used in the experiment.

The absorption spectra measurements were carried out on a Purkinje General TU-1901 spectrophotometer in 1 nm steps. All of the experiments were performed at room temperature in a dark room.

0.0007 g of all-*trans*-β-carotene is diluted in 10 ml benzene to study the influence of the liquid temperature on RSCS, 1 ml of mixture is instilled into 9 ml dimethyl sulfoxide.

0.0013 g of all-*trans*-β-carotene is diluted by 20 ml cyclohexane to study the influence of the sol-

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vent density on SCRS, we instill 1 ml of solution into 9 kinds of solvents, namely carbon disulfide, benzene, carbon tetrachloride, acryl acid, dichloromethane, diethylamine, chloroform, tetrachloroethylene and normal octane, of 9 ml in each case. We prepare the concentration of all-*trans*-β-carotene in solutions at 1.2×10^{-5} M (1 M = 1 mol/dm^3).

We dissolve all-*trans*-β-carotene in disulfide to study the influence of the solvent concentration on RSCS, appropriate amount of it is dissolved in 1 ml n-hexane (A.R. purity≥99.0%), and then diluted by disulfide. Further dilutions by disulfide are performed to give fresh solutions with various concentrations ranging from 10^{-6} to 10^{-11} M.

3. Results and discussion

3.1. Influence of solvent temperature on the all-*trans*-β-carotene RSCS

Raman spectra of all-*trans*-β-carotene in dimethyl sulfoxide solution were measured with the temperature changing, the temperature range was from 25 °C to 73 °C. The results are shown in Fig. 1.

We can obtain the RSCS of all-*trans*-β-carotene in dimethyl sulfoxide at different temperatures using Eqs. (1) and (2),[10,11] as shown in Table 1,

$$\sigma_{\rm S} = \sigma_{\rm R} \cdot \left(\frac{I_{\rm S}}{I_{\rm R}}\right) \left[\frac{v_0\left(v_0 - v_{\rm R}\right)^3}{v_0\left(v_0 - v_{\rm S}\right)^3}\right] \left(\frac{C_{\rm R}}{C_{\rm S}}\right) L\left(v_0\right), \quad (1)$$

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

where $\sigma_{\rm R}$ is benzene 992 cm^{-1} band RSCS, the subscript S is for 1520 cm^{-1} and 1155 cm^{-1} Raman band of all-*trans*-β-carotene, $C_{\rm R}$ and $C_{\rm S}$ are the molar concentrations of benzene and all-*trans*-β-carotene, respectively. $I_{\rm S}/I_{\rm R}$ is the Raman intensity ratio of the 992 cm^{-1} band of benzene relative to the 1520 cm^{-1} and 1155 cm^{-1} bands of all-*trans*-β-carotene. v_0 is the incident excitation beam wave number (cm^{-1}), $L(v_0)$ is the local field correction factor based on Onsager's theory, and n is the refractive index of the solvent.

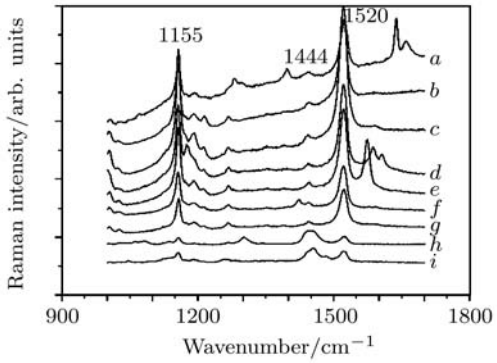


Fig. 1. Raman spectra of all-*trans*-β-carotene in dimethyl sulfoxide at different temperatures curve *a*: 73 °C, curve *b*: 58 °C, curve *c*: 49 °C, *d*: 40 °C, curve *e*: 25 °C. Benzene 992 cm^{-1} Raman line acted as the internal standard.

Table 1. RSCS of all-*trans*-β-carotene CC bonds in solvent at different temperatures.

temperature /°C	RSCS of C–C /10^{-23} cm$^2\cdot$molecule$^{-1}\cdot$Sr^{-1}	RSCS of C–C /10^{-23} cm$^2\cdot$molecule$^{-1}\cdot$Sr^{-1}
25	5.9	6.5
28	5.8	6.6
31	6.1	6.4
34	5.8	6.2
37	5.9	6.3
40	5.8	6.2
43	5.7	6.3
46	5.6	6.2
49	5.6	6.1
52	5.7	6.2
55	5.5	6.1
58	5.4	6.1
61	5.7	6.1
64	5.3	6.1
67	5.4	6.1
70	5.4	6.1
73	5.3	5.8

Figure 2 shows the linear relationship between the all-*trans*-β-carotene CC bond RSCS and the temperature. The speed of molecular motion becomes faster, and makes the entropy increasing, which results in the solvent instability. The descending ordered structure of all-*trans*-β-carotene makes the coherent weakly damped CC bond vibration weaken, so RSCS is reduced. The alteration of scattering molecular density, statistical distribution and refractive index are the elements causing the Raman intensity variation.[12] In addition, the Raman line width of CC bond increased and showed blue shift with the temperature increasing.

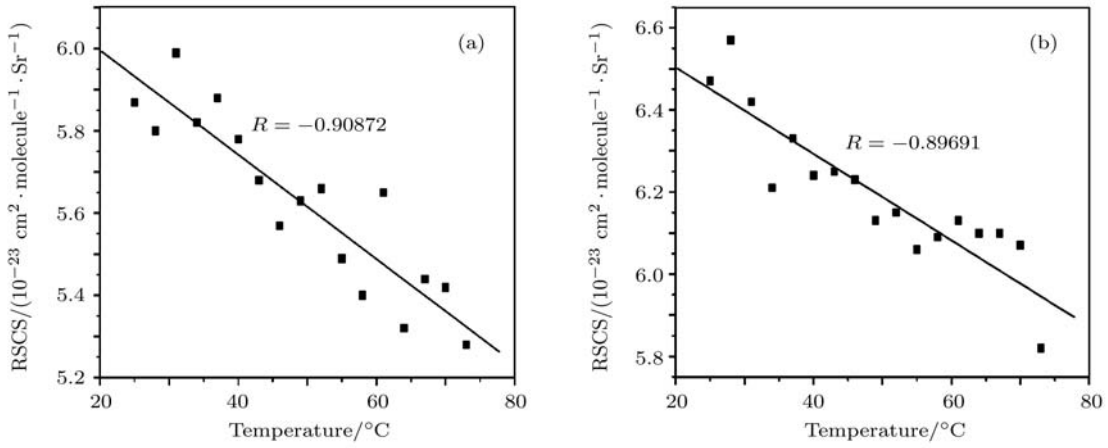


Fig. 2. The relationship of C–C(a) and C–C(b) RSCS with the temperature changing.

3.2. Influence of solvent density on the all-*trans*-β-carotene RSCS

Raman spectra of all-*trans*-β-carotene in 9 solvents under the 514.5 nm laser excitation are shown in Fig. 3.

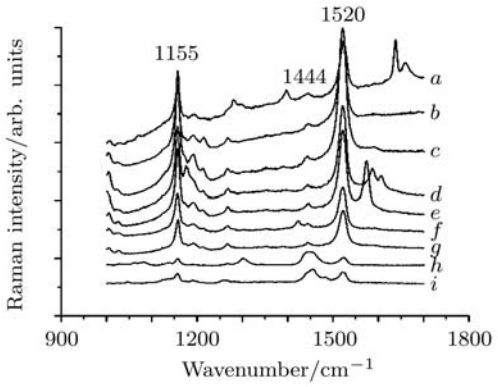


Fig. 3. Raman spectra of all-*trans*-β-carotene in 9 solvents, curve *a*: acryl acid, curve *b*: chloroform, curve *c*: disulfide, curve *d*: benzene, curve *e*: tetrachloroethylene curve *f*: dichloromethane, curve *g*: carbon tetrachloride, curve *h*: normal octane, curve *i*: diethylamine. The excitation power is 4.3 mW. Cyclohexane 1444 cm^{-1} Raman line acted as the internal standard.

The RSCS of all-*trans*-β-carotene in 9 solvents were calculated by the following expressions, the RSCS values are listed in Table 2.

We make a sub-peak processing when the SRCS of all-*trans*-β-carotene in normal octane and diethylamine was calculated, because the solvent Raman bands are superimposed on the reference band. Because the SRCS is related with the pump wavelength, and the 514.5 nm pump wavelength do not lie within the strict electron absorption peaks of all-*trans*-β-carotene in these 9 solvents, the Raman scattering of all-*trans*-β-carotene in these 9 solvents are not all the resonant Raman scattering. We make a wavelength revisal for the SRCS to define the relationship between SRCS and solvent density. According to the Albrench theory,[13] the SRCS σ of all-*trans*-β-carotene can be determined by

$$\sigma = \frac{A}{(V_0 - V_e)^2 + \Gamma_e^2}, \tag{3}$$

where σ is the SRCS, A is constant (scale factor), Γ_e is the damping parameter of electron absorption band (0–0), V_0 and V_e are the incident excitation beam wave number and electronic absorption peak frequency, respectively. We revised the SRCS of all the samples, because the solution volume that is operated on by the laser is the same; otherwise, the number of all-*trans*-β-carotene molecules we measured is different owing to the different solvent density. We make tetrachloroethylene the benchmark for density of the revisal. Table 3 shows the SRCS of all-*trans*-β-carotene in 9 solvents after wavelength and molecule number revisal.

Table 2. SRCS of all-*trans*-β-carotene in 9 solvents with the 514.5 nm laser excitation.

solvent	density /kg · m^{-3}	C–C (1155 cm^{-1}) /10^{-23} cm^2 · molecule^{-1} · Sr^{-1}	C–C (1520 cm^{-1}) /10^{-23} cm^2 · molecule^{-1} · Sr^{-1}
tetrachloroethylene	1.6226	31.58	38.78
carbon tetrachloride	1.5940	28.31	35.15
chloroform	1.4916	36.46	44.05
dichloromethane	1.3266	30.91	37.82
carbon disulfide	1.2600	51.44	63.99
acryl acid	1.0520	15.16	19.07
benzene	0.8800	15.64	20.42
normal octane	0.7080	39.82	59.51
diethylamine	0.7056	34.74	52.73

Table 3. SRCS of all-*trans*-β-carotene in 9 solvents after the wavelength and molecule number revisal.

solvent	Density /kg · m^{-3}	C–C (1155 cm^{-1}) /10^{-23} cm^2 · molecule^{-1} · Sr^{-1}	C–C (1520 cm^{-1}) /10^{-23} cm^2 · molecule^{-1} · Sr^{-1}
tetrachloroethylene	1.6226	8.42	10.34
carbon tetrachloride	1.5940	7.69	9.55
chloroform	1.4916	7.53	9.12
dichloromethane	1.3266	7.17	8.77
carbon disulfide	1.2600	6.78	7.90
acryl acid	1.0520	5.67	7.13
benzene	0.8800	4.58	5.98
normal octane	0.7080	2.53	3.78
diethylamine	0.7056	2.31	3.51

From Table 3, we obtain the linearly relationship of all-*trans*-β-carotene CC bond RSCS with the solvent density, as shown in Fig. 4.

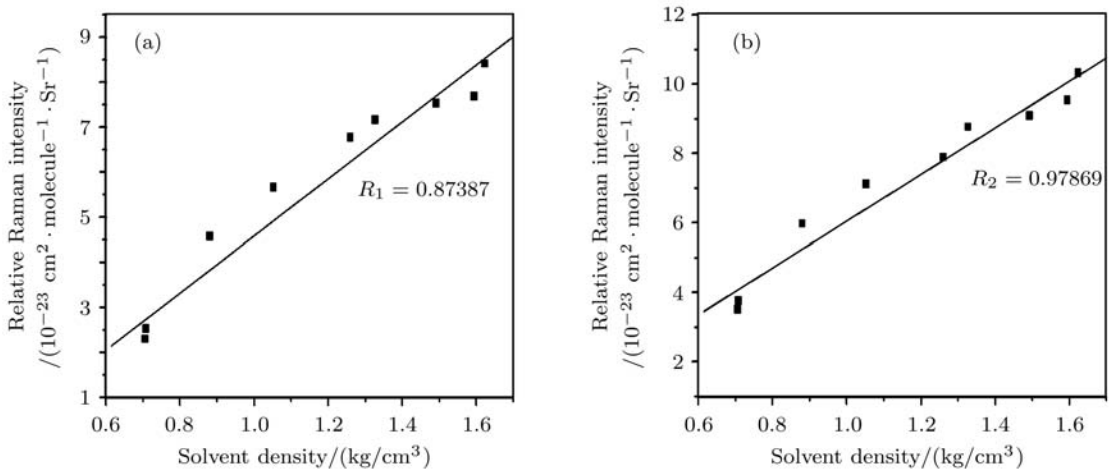


Fig. 4. The relationship of all-*trans*-β-carotene C–C (a) and C–C (b) bond SRCS with the solvent density.

The mechanism is that all-*trans*-β-carotene in large volume density influenced by perturbation is small, with the high structured order, extended π electronic delocalization and strong coherent weakly damped CC bond vibrating properties,[9] it is lead to have a large RSCS.

3.3. Influence of solvent concentration on the all-*trans*-β-carotene RSCS

Raman spectra of all-*trans*-β-carotene in CS_2 solution at low concentrations (10^{-6}–10^{-11}M) with the baseline correction are shown in Fig. 5.

We obtained the RSCS of all-*trans*-β-carotene in disulfide simultaneous from Eqs. (1) and (2). The results are shown in Table 4, and the relationship is shown in Fig. 6.

The increase tendency of the RSCS as the solution concentration decreases is similar to the presentation of the equation

$$\sigma_{\mathrm{R}}(C) = A\exp\left(\frac{-C}{B}\right) + D, \tag{4}$$

where A, B and D are the fitted parameters, σ_{R} represents the RSCS of the 1520 and 1155 cm^{-1} of all-*trans*-β-carotene and C is the solution concentration. The fitting parameters are $A = 38838$, $B = 1.9\times10^{-10}$, $D = 287$, correlation coefficient $R = 0.995$, and $A = 1869$, $B = 2.0\times10^{-9}$, $D = 36$, correlation coefficient $R = 0.986$, for the 1520 cm^{-1} and 1155 cm^{-1}, respectively.

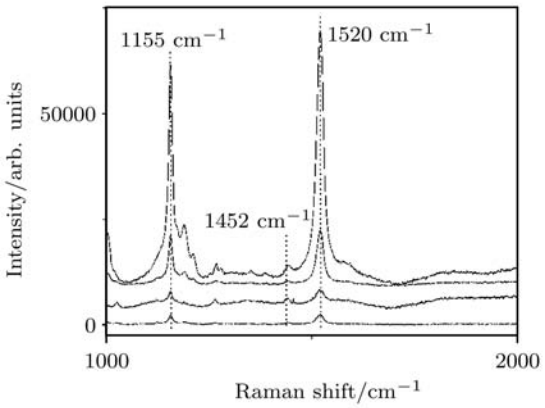


Fig. 5. Raman spectra of all-*trans*-β-carotene in disulfide solutions at low concentrantions from 10^{-6} to 10^{-11} M (curve *a*: 10^{-6}M; curve *b*: 10^{-8}M; curve *c*: 10^{-10}M; curve *d*: 10^{-11}M) The excitation power was 13.6 mW. Cyclohexane 1444 cm^{-1} Raman line acted as the internal standard.

Table 4. The RSCS for C–C and C–C stretching modes of all-*trans*-β-carotene in disulfide solutions at various concentrations calculated by using peak area ratios.

concentration/M	C–C (1520 cm^{-1}) /10^{-24}cm$^2\cdot$molecule$^{-1}\cdot$Sr^{-1}	C–C (1155 cm^{-1}) /10^{-24}cm$^2\cdot$molecule$^{-1}\cdot$Sr^{-1}
8×10^{-6}	1.73	1.99
8×10^{-7}	9.05	10.3
8×10^{-8}	30.1	31.7
8×10^{-9}	200	310
8×10^{-10}	1320	1810
8×10^{-11}	–	26300

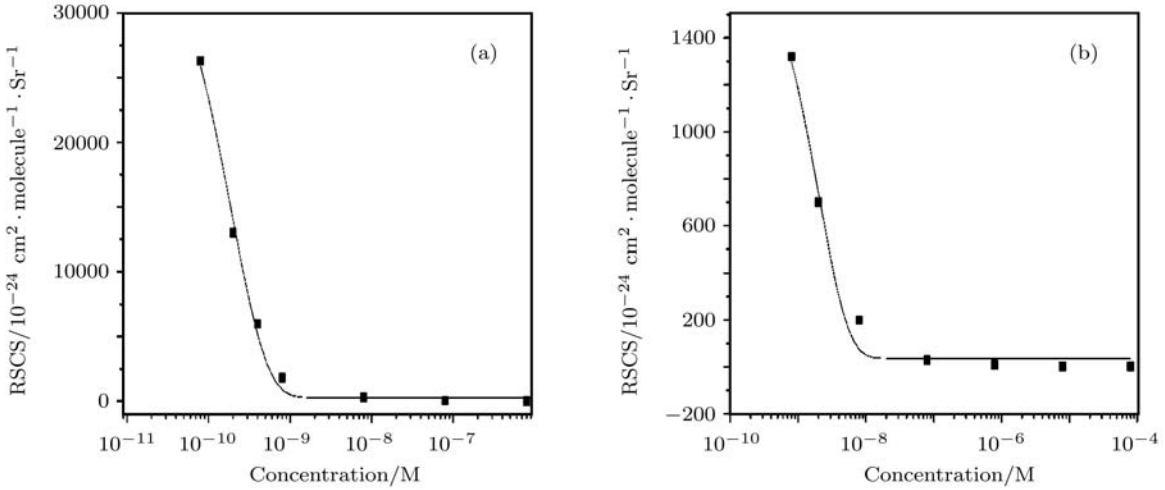


Fig. 6. The relative changing tendency RSCS for C–C (a) and C–C (b) stretching mode of all-*trans*-β-carotene in disulfide solutions with the concentration decreasing.

With the concentration decreasing, the number of all-*trans*-β-carotene molecules decreased, intermolecular distance R_{l} increased and intermolecular interaction of all-*trans*-β-carotene weakened with $1/R_{\mathrm{l}}^6$. In addition, the number of disulfide molecules located at single all-*trans*-β-carotene molecule increased, so the large density of disulfide made the disturbance of external environment reduced, and uniform forces acted

on CC bonding of all-*trans*-β-carotene, which lead to the rise of the degree of ordered structure of all-*trans*-β-carotene molecule. The lower the concentration is, the more rapid the enhancement in induced degree of structural order of all-*trans*-β-carotene is. All-*trans*-β-carotene has the high ordered structure, enhanced π electronic delocalization, which lead to the enhancement of coherent weakly damped CC bond vibrating properties, and made the RSCS large.

4. Conclusion

The RSCS is extremely high in the short-chain polymer all-*trans*-β-carotene in liquid phase. Coherent weakly damped CC bond vibrating property generated by the structured order is an important factor. The low temperature, large solvent density and low concentration make the ordered structure extremely high. We can obtain large RSCS of all-*trans*-β-carotene in solvent when the solvents satisfy the above-mentioned requirement.

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