# Effects of the structural order of canthaxanthin on the Raman scattering cross section in various solvents: A study by Raman spectroscopy and *ab initio* calculation*

Wu Nan-Nan(吴楠楠)[a)b)], Li Zuo-Wei(里佐威)[b)], Liu Jing-Yao(刘靖尧)[c)], and OuYang Shun-Li(欧阳顺利)[a)†]

[a)] *Key Laboratory of Integrated Exploitation of Bayan Obo Multi-Metal Resources, Inner Mongolia University of Science & Technology, Baotou* 014010, *China*

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

[c)] *Institute of Theoretical Chemistry, State Key Laboratory of Theoretical and Computational Chemistry, Jilin University, Changchun* 130023, *China*

(Received 27 January 2012; revised manuscript received 24 April 2012)

In this work, we measure the Raman scattering cross sections (RSCSs) of the carbon–carbon (CC) stretching vibrational modes of canthaxanthin in benzene, acetone, *n*-heptane, cyclohexane, and *m*-xylene. It is found that the absolute RSCS of CC stretching mode of canthaxanthin reaches a value of $10^{-24}$ cm$^2$·molecule$^{-1}$·sr$^{-1}$ at $8\times10^{-5}$ M, which is 6 orders of magnitude larger than general RSCS ($10^{-30}$ cm$^2$·molecule$^{-1}$·sr$^{-1}$), and the RSCSs of canthaxanthin in various solvents are very different due to the hydrogen bond. A theoretical interpretation of the magnetic experimental results is given, which is introduced in a qualitative nonlinear model of coherent weakly damped electron–lattice vibration in the structural order of polyene chains. In addition, the optimal structure and the bond length alternation (BLA) parameter of canthaxanthin are calculated using quantum chemistry calculation (at the b3lyp/6-31g (d, p) level of theory). The theoretical calculations are in good agreement with the experimental results. Furthermore, the combination of Raman spectroscopy and the quantum chemistry calculation study would be a quite suitable method of studying the structures and the properties of the $\pi$-conjugated systems.

**Keywords:** Raman spectroscopy, the bond length alternation (BLA) parameter, quantum chemistry calculation, canthaxanthin

**PACS:** 31.15.A–, 31.70.Dk, 33.20.Fb **DOI:** 10.1088/1674-1056/21/10/103101

## 1. Introduction

During the last years, the physics of elementary excitations in polyene chains containing a $\pi$-conjugated system has attracted the particular attention of researchers.[1–3] Canthaxanthin is the chemically simple $\pi$-conjugated polyene (Fig. 1), in which the polyene chain consists of a sequence of carbon–carbon (CC) bonds ($\cdots$–C=C–C=$\cdots$), characterized by a strong electron–phonon (e-ph) coupling due to delocalized $\pi$ electrons. The density of mobile $\pi$-electrons between adjacent carbon sites in the polyene chain strongly modulates the strength of their covalent bonding giving a high e-ph coupling and an effective nonlinearity for the lattice motion.[1]

Knowledge of the spectroscopic characteristics of the polyene molecules in solution is a necessary prerequisite for understanding their functions in complex natural or artificial systems, so the study of solvent effects on these polyene molecules is of great significance. There have been numerous experimental and theoretical studies of polyenes in different solutions, but most of them focus on the solvent effects on the ground state and the excited state in absorption spectra and are investigated in connection with the effect of phonon frequency dispersion with exciting photon energy in Raman spectra.[2–5] Much less attention is paid to Raman intensity studies in $\pi$-conjugated systems.

*Project supported by the National Natural Science Foundation of China (Grant Nos. 11004252 and 10974067) and the National Basic Research Program of China (Grant No. 2012CB722802).

†Corresponding author. E-mail: ouyang08@mails.jlu.edu.cn

© 2012 Chinese Physical Society and IOP Publishing Ltd

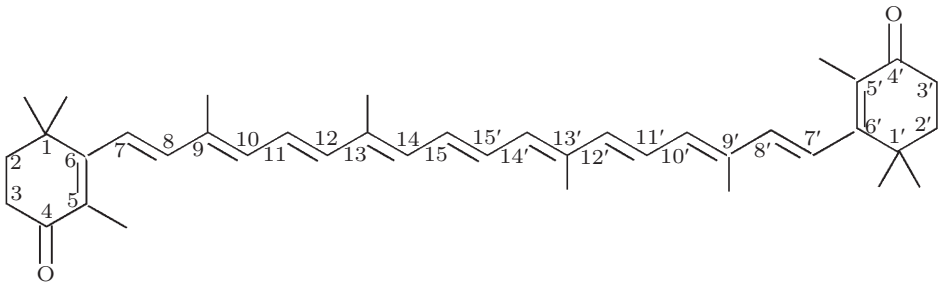



**Fig. 1.** Structure and numbering of canthaxanthin.

During the past decade, we have used the Raman spectra of polyenes to perform a series of studies in the respect.[6−8] The main work is to investigate the Raman scattering cross section (RSCS) of $\beta$-carotene. Because RSCS is an important parameter in the study and application of the Raman spectroscopy. It relates not only to the incident frequency and the scattered molecular structure but also to the environment where the scattered molecule are located. It is usually obtained by comparing the Raman spectrum intensity of an unknown molecule with that of a standard molecule with a known cross-section. In our previous work, Tian *et al.*[6] proved that RSCS of aqueous $\beta$-carotene molecule, which has 11 conjugated double bonds, was high RSCS. Recently, we found that the RSCSs of all-trans-$\beta$-carotene are extremely high in the nonpolar solvent ($CS_2$), and the RSCS of C=C stretching mode of all-trans-$\beta$-carotene reaches a value of $2.6\times10^{-20}$ cm$^2$·molecule$^{-1}$·sr$^{-1}$ at $8\times10^{-11}$ M, which is four orders of magnitude larger than the value at $8\times10^{-6}$ M.[8] In the present paper, we measure the Raman spectra of canthaxanthin in polar solutions and nonpolar solutions and compare the solvent effects on the anomalously high RSCS of two representative Raman bands in these solvents. Additionally, in order to explain the solvent effects on the anomalously high RSCS, we use a coherent qualitative nonlinear model, which was proposed by Paraschuk and Kobryanskii.[1] In particular, we use a combination of Raman spectroscopy and quantum chemistry calculations to study the structure of canthaxanthin. The combination of experimental Raman data with *ab initio* calculation leads to a better understanding of the studied hydrogen-bonded complexes.[9]

# 2. Materials and methods

## 2.1. Samples and procedures

The canthaxanthin is purchased from J & K Chemical LTD, and it is stored at −4 °C in the dark to avoid exposure to moisture and light, and used without further purification. The canthaxanthin is dissolved in solvents. The solvents are benzene, acetone, *n*-heptane, *n*-haxane, *m*-xylene (analytical grade) separately. In all of the experiments, fresh solution is used immediately to avoid degradation.

## 2.2. Spectroscopic methods

The micro-Raman spectrometer (Renishaw InVia Raman microscope) is equipped with an argon ion laser operating at 514.5 nm (Spectra Physics 163-M42) for excitation. A 20× objective (Leica DMLM 0.12NA) is used both for the laser illumination and detection of the backscattered Raman light. A laser power of 4.6 mW is used to collect all Raman spectra. The exposure time is 10 s and resolution is 1.4 cm$^{-1}$.

The absorption spectral measurements are carried out on a Purkinje General TU-1901 spectrophotometer in steps of 0.5 nm. All the experiments are performed at room temperature in a dark room.

## 2.3. Computational methods

The geometries of the monomers and their various hydrogen bonded complexes are optimized using the hybrid density functional B3LYP method in conjunction with the 6-31+G (d, p) basis set. Vibrational frequency calculations are performed at the same level of theory to verify whether they are minima with all positive frequencies. All calculations are performed with the Gaussian 03 program package.[10]

# 3. Results

## 3.1. Micro-Raman spectroscopy

The Raman spectra of canthaxanthin in various solvents are shown in Fig. 2. The Raman spectrum bands at 1444 $cm^{-1}$, 1156 $cm^{-1}$, and 1518 $cm^{-1}$ originate from the scissor bending vibration of the methylene groups of *n*-hexane molecules, from the carbon–carbon single bond and the carbon–carbon double-bond stretch vibration of the conjugated backbone of canthaxanthin molecules, respectively.[11,12]

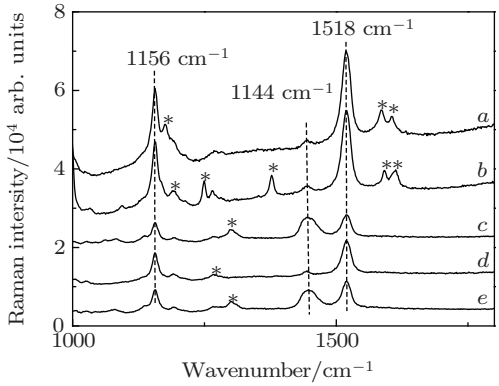



**Fig. 2.** Raman spectra of canthaxanthin in acetone benzene (curve *a*), *m*-xylene (curve *b*), cyclohexane (curve *c*), n-heptane (curve *d*), and acetone (curve *e*). Asterisks indicate Raman bonds from solvents.

## 3.2. Calculation of RSCS

The 1444-$cm^{-1}$ Raman band of *n*-hexane is selected as an internal standard, and the RSCS is calculated by the following expression:[8,12,13]

$$(\sigma_{\mathrm{R}})_X = (\sigma_{\mathrm{R}})_{1444}\left(\frac{I_X}{I_{1444}}\right)\left[\frac{\nu_0\left(\nu_0-1444\right)^3}{\nu_0\left(\nu_0-X\right)^3}\right] \times \left(\frac{C_{1444}}{C_X}\right)L\left(\nu_0\right), \quad (1)$$

where $\sigma_{\mathrm{R}}$ is the RSCS, the subscripts $X$ refers to the Raman band of canthaxanthin, $C_{1444}$ and $C_X$ are the molar concentrations of *n*-hexane and canthaxanthin, $I_X/I_{1444}$ is the Raman intensity ratio of the 1444 $cm^{-1}$ band of *n*-hexane to the Raman band of canthaxanthin, $v_0$ is the wavenumber of the incident excitation beam, $L(v_0)$ is the local field correction factor based on Onsager's model and is expressed as

$$L\left(\nu_0\right) = \frac{\sigma_{mn}\left(\mathrm{sol}\right)}{\sigma_{mn}\left(\mathrm{vapor}\right)} = \left\{\frac{n^2\left(\nu_0\right)+2}{\left[\frac{n}{n_{\mathrm{sol}}}\right]^2+2}\right\}^4, \quad (2)$$

with $\sigma_{mn}$ (sol) and $\sigma_{mn}$ (vapor) representing the RSCSs of the vibrational transition $n \leftarrow m$ in solution phase and in vapour phase, respectively, $n$ ($\nu_0$) being the refractive index of neat liquid at the excitation frequency ($\nu_0$), and $n_{\mathrm{sol}}(\nu_0)$ denoting the refractive index of the solution at the excitation frequency. Here, the refractive index of the solution ($n$) is a volume-weighted average value of those of its components.

According to Eq. (1), the absolute RSCSs of C=C and C–C stretching modes of canthaxanthin in various solutions at $10^{-5}$ M are calculated. The values of the absolute RSCSs of canthaxanthin are summarized in Table 1. As can be clearly seen, the absolute RSCS of the CC stretching mode of canthaxanthin reaches a value of $10^{-24}$ $cm^2 \cdot molecule^{-1} \cdot sr^{-1}$ at $8\times10^{-5}$ M, which is 6 orders of magnitude larger than general RSCS ($10^{-30}$ $cm^2 \cdot molecule^{-1} \cdot sr^{-1}$), and the RSCSs of canthaxanthin in various solvents are very different. The solvent effect influence on the property of a $\pi$-conjugated chain of canthaxanthin is quite intriguing, which will be discussed in the forthcoming sections.

**Table 1.** The RSCSs for C=C and C–C stretching modes of canthaxanthin in various solvents calculated by using peak-to-area ratios.

| Solvent | RSCS ($10^{-24}$ $cm^2 \cdot molecule^{-1} \cdot sr^{-1}$) | |
|---|---|---|
| | C=C (1518 $cm^{-1}$) | C–C (1156 $cm^{-1}$) |
| Acetone | 2.4 | 1.6 |
| *n*-heptane | 9.8 | 6.3 |
| Cyclohexane | 13.5 | 11.3 |
| *m*-xylene | 18.6 | 16.5 |
| Benzene | 19.5 | 17.2 |

## 3.3. UV-Vis absorption spectroscopy

The UV-Vis absorption spectra of canthaxanthin are generally shaped by a strong band in a range from 350 nm to 600 nm. This absorption band is attributed to the $A_g^- \rightarrow B_g^-$ transition. Figure 3 shows the UV-Vis absorption spectra of canthaxanthin in the solvents, and listed in Table 2 are the wavelengths of the vibronic $A_g^- \rightarrow B_g^-$ transitions. In solvents, the absorption spectra of canthaxanthin exhibit poorly-resolved vibrational structures. Thus, the vibronic $A_g^- \rightarrow B_g^-$ transition of the canthaxanthin shows the three components extracted from a curve-fitting analysis (see Fig. 3).

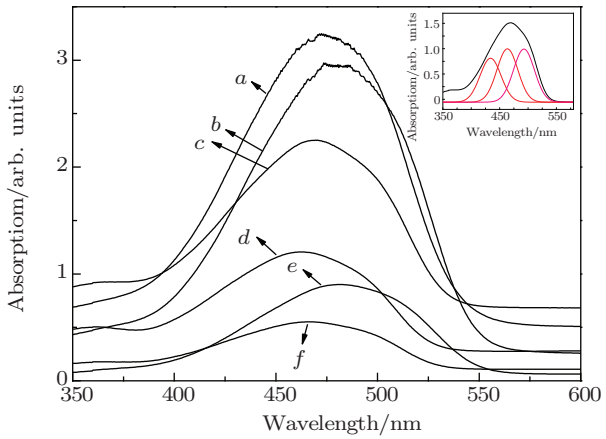



**Fig. 3.** (colour online) UV-Vis absorption spectra of canthaxanthin in acetone (curve *a*), *m*-xylene (curve *b*), cyclohexane (curve *c*), *n*-heptane (curve *d*), and benzene (curve *e*). The inset shows the results of the curve fitting for the vibronic $A_g^- \rightarrow B_g^-$ transition.

**Table 2.** Wavelength (in nm) of electronic absorption peaks of canthaxanthin in various solvents.

| Solvent | $A_g^- \rightarrow B_g^-$ | | |
|---|---|---|---|
| | (0–2) | (0–1) | (0–0) |
| Acetone | 442 | 472.5 | 502.5 |
| *n*-heptane | 433.5 | 463.5 | 492.5 |
| Cyclohexane | 440.5 | 470.5 | 501 |
| *m*-xylene | 451 | 480.5 | 510.5 |
| Benzene | 451 | 481.5 | 512 |

## 3.4. Quantum chemistry calculation

Selected optimized geometric parameters of the molecules are listed in Table 3. As seen from Fig. 4, a hydrogen bond occurs between the H atom of the solvent molecule and the O atom of canthaxanthin molecule. The canthaxanthin is strongly conjugated, with the difference between singly and double bonds being small in the middle of the polyene chain. The degree of conjugation in a molecule can be evaluated by means of the bond length alternation (BLA) parameter, which is defined as the difference in total length between single bonds (C–C) and double bonds (C=C). The BLA parameter increases as the conjugation degree decreases. We calculate the BLA parameter from C5 to $C_8'$ at the other end of the molecule. The BLA parameters of canthaxanthin and canthaxanthin in solvents are listed in Table 3. As seen from Table 3, the canthaxathin has larger BLA parameters than the canthaxanthin in solvents, indicating a low degree of conjugation in the anthaxanthin compared with the anthaxanthin in solvents.

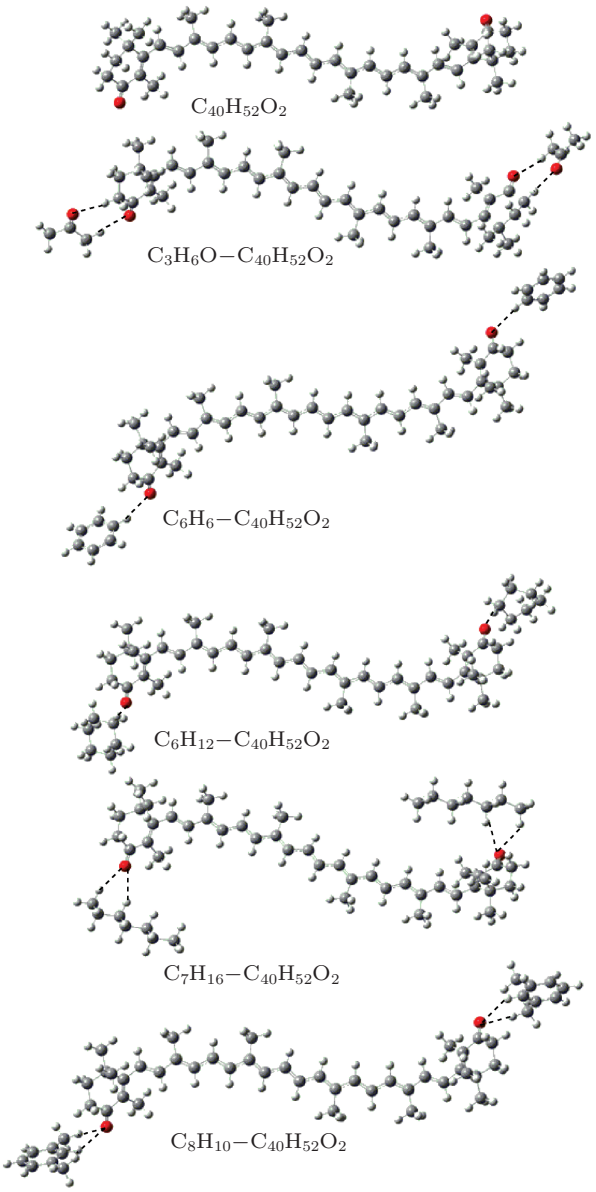



**Fig. 4.** (colour online) Optimized structures of canthaxanthin and the hydrogen-bonded complexes of canthaxanthin, obtained by quantum chemistry calculations, with the broken lines representing the hydrogen bonds.

**Table 3.** Values of selected geometric parameter (Å) of the canthaxanthin (a) and canthaxanthin in solvents optimized at the b3lyp/6-31g (d, p) level.

| | $C_{40}H_{52}O_2$ | $C_3H_6O$ | $C_6H_6$ | $C_6H_{12}$ | $C_7H_{16}$ | $C_8H_{10}$ |
|---|---|---|---|---|---|---|
| A | 1.488 | 1.48736 | 1.48557 | 1.48578 | 1.48531 | 1.48481 |
| B | 1.37046 | 1.37051 | 1.37149 | 1.37173 | 1.37147 | 1.37203 |
| C | 1.46729 | 1.46751 | 1.46628 | 1.46578 | 1.46621 | 1.46579 |
| D | 1.35771 | 1.35754 | 1.35822 | 1.35866 | 1.35832 | 1.35852 |

**Table 3.** (*Continued*).

| | $C_{40}H_{52}O_2$ | $C_3H_6O$ | $C_6H_6$ | $C_6H_{12}$ | $C_7H_{16}$ | $C_8H_{10}$ |
|---|---|---|---|---|---|---|
| E | 1.45029 | 1.45047 | 1.44982 | 1.44976 | 1.44975 | 1.44957 |
| F | 1.36996 | 1.36992 | 1.37025 | 1.37037 | 1.3703 | 1.3704 |
| G | 1.43295 | 1.433 | 1.43277 | 1.43256 | 1.43266 | 1.43266 |
| H | 1.36505 | 1.36501 | 1.36514 | 1.36522 | 1.36515 | 1.36518 |
| I | 1.44172 | 1.4417 | 1.44156 | 1.44162 | 1.44164 | 1.44154 |
| J | 1.37412 | 1.37407 | 1.37421 | 1.37427 | 1.37428 | 1.37425 |
| K | 1.42755 | 1.42776 | 1.4276 | 1.42745 | 1.42752 | 1.42753 |
| L | 1.36862 | 1.36856 | 1.36863 | 1.3687 | 1.36865 | 1.36865 |
| M | 1.42755 | 1.42769 | 1.42755 | 1.42751 | 1.42757 | 1.42753 |
| N | 1.37411 | 1.37418 | 1.37428 | 1.37419 | 1.3742 | 1.37425 |
| O | 1.44175 | 1.44188 | 1.44158 | 1.44154 | 1.44154 | 1.44154 |
| P | 1.36503 | 1.36496 | 1.36516 | 1.36522 | 1.36518 | 1.36518 |
| Q | 1.43299 | 1.43305 | 1.43271 | 1.43267 | 1.43269 | 1.43266 |
| R | 1.36989 | 1.36997 | 1.37039 | 1.37024 | 1.37028 | 1.3704 |
| S | 1.45072 | 1.45095 | 1.44964 | 1.44978 | 1.44971 | 1.44956 |
| T | 1.35758 | 1.35755 | 1.35847 | 1.35841 | 1.35845 | 1.35853 |
| U | 1.46494 | 1.46495 | 1.46606 | 1.46618 | 1.46603 | 1.46578 |
| V | 1.37113 | 1.37098 | 1.37169 | 1.37152 | 1.37179 | 1.37203 |
| W | 1.48934 | 1.48889 | 1.4854 | 1.48647 | 1.48495 | 1.48481 |
| $BLA_{b-s}$ | 0.75786 | 0.66929 | 0.65174 | 0.65007 | 0.65246 | 0.64952 |

# 4. Discussion

Using 514.5 excitation, the Raman spectra of canthaxanthin are resonance Raman spectra, so the RSCS is relative to UV-Vis absorption band. The resonance Raman effect has an influence on the RSCS of canthaxanthin, notwithstanding it is not the major cause. According to the Albrench theory, the RSCS of canthaxanthin can be determined by

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

where $\sigma$ is the RSCS; $A$ is a constant (scale factor); $\Gamma_e$ 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. According to Eq. (3), the absolute RSCSs of C=C and C–C stretching modes of canthaxanthin are listed in Table 4. As shown in Table 4, the RSCS values of canthaxanthin are different in various solvents. We suggest that this difference is due to the hydrogen bond, which is formed between the canthaxanthin molecule and the solvent molecule. Because of the hydrogen bond, the CC bonding of canthaxanthin is forced, which could influence the degree of structural order of the canthaxanthin molecule. Therefore, the electronic delocalization is affected in the canthaxanthin chain by the unequal degree of structural order of canthaxanthin in various solvents. According to previous report by Paraschuk and Kobryanskii,[1] i.e., a qualitative nonlinear model of coherent weekly damped electron–lattice vibrations, the degree of delocalization of $\pi$ electron increases (decreases), thus influencing the density of mobile $\pi$ electrons between adjacent carbon sites in the canthaxanthin chain and so strongly (weakly) modulating the strength of their covalent bonding that gives rise a high electron–phonon coupling, which results in the fact that the RSCS values of canthaxanthin are different in various solvents. In this study, these results are supported by our calculated results. As shown in Fig. 3, the hydrogen-bonded complex of canthaxanthin with two solvent molecules is calculated from their configurations. In these cases, the two O-atoms of the reference molecule canthaxanthin form hydrogen bonds with the H atom of two solvent molecules. In addition, it can be seen from Table 3 that the degree of structural order of the canthaxanthin molecule changes due to the hydrogen bond. As seen from Table 3, the BLA parameters of the hydrogen-bonded complex of canthaxanthin are in the order, canthaxanthin > acetone > *n*-heptane > cyclohexane > benzene > *m*-xylene. Thus, it indicates

that the degrees of conjugation of the canthaxathin in solvents are in the order, *m*-xylene > benzene > cyclohexane > *n*-heptane > acetone. On the other hand, the RSCS values of canthaxanthin in various solvents are in the order, *m*-xylene > benzene > cyclohexane > *n*-heptane > acetone (see Table 4). Therefore, it can be concluded that the theoretical chemistry calculations are in very good agreement with the experimental results.

**Table 4.** Revised RSCSs for C=C and C–C stretching modes of canthaxanthin in polar and nonpolar solvents.

| Solvent | RSCS ($10^{-24}$ cm$^2$·molecule$^{-1}$·sr$^{-1}$) | |
|---|---|---|
| | C=C (1518 cm$^{-1}$) | C–C (1156 cm$^{-1}$) |
| Acetone | 2.8 | 1.9 |
| *n*-heptane | 10.7 | 7.5 |
| Cyclohexane | 12.8 | 10.7 |
| *m*-xylene | 17.9 | 15.2 |
| Benzene | 16.5 | 14.6 |

## 5. Conclusion

The Raman spectra of canthaxanthin in various solvents are obtained at $10^{-5}$ M, and the absolute RSCSs for C=C and C–C stretching modes in various solvents are determined. It is found that the absolute RSCSs of canthaxanthin in various solvents are very different due to the hydrogen bond. According to the coherent model, the degree of structural order of the canthaxanthin is affected due to the hydrogen bond in solvent, which leads to the very different RSCSs of canthaxanthin. Additionally, the magnetic experimental results are confirmed by quantum chemistry calculation. The results reported here are important for better understanding that the hydrogen bonds play a role in influencing the properties of the molecule containing $\pi$-conjugated system.

## References


[1] Paraschuk D Y and Kobryanskii V M 2001 *Phys. Rev. Lett.* **87** 207402

[2] Guo J D, Luo Y and Himo F 2002 *Chem. Phys. Lett.* **366** 73

[3] Tschirner N, Schenderlein M, Brose K, Schlodder E, Mroginski M A, Thomsen C and Hildebrandt P 2009 *Phys. Chem. Chem. Phys.* **11** 11471

[4] Zigmantas D, Hiller R G, Sharples F P, Frank H A, Sundström V and Polívka T 2004 *Phys. Chem. Chem. Phys.* **6** 3009

[5] Köpsel C, Möltgen H, Schuch H, Auweter H, Kleinermanns K, Martin H D and Bettermann H 2005 *J. Mol. Struct.* **750** 109

[6] Tian Y J, Zhang L Y, Zuo J, Li Z W, Gao S Q and Lu G H 2007 *Antal. Chim. Acta* **581** 154

[7] Tian Y J, Zuo J, Zhang L Y, Li Z W, Gao S Q and Lu G H 2007 *Appl. Phys.* B **87** 727

[8] OuYang S L, Sun C L, Zhou M, Li Z L, Men Z W, Li D F, Li Z W, Gao S Q and Lu G H 2010 *J. Raman Spectrosc.* **41** 1650

[9] OuYang S L, Wu N N, Sun C L, Liu J Y, Li Z W and Gao S Q 2010 *Chin. Phys.* B **19** 093103

[10] Frisch M J, Truck G W, Schlegel H B, Scuseria G E, Robb M A, Cheeseman J R, Zakrzewski V G, Montgomery J A Jr, Stratmann R E, Burant J C, Dapprich S, Millam J M, Daniels A D, Kudin K N, Strain M C, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson G A, Ayala P Y, Cui Q, Morokuma K, Malick D K, Rabuck A D, Raghavachari K, Foresman J B, Cioslowski J, Ortiz J V, Boboul A G, Stefnov B B, Liu G, Liaschenko A, Piskorz P, Komaromi L, Gomperts R, Martin R L, Fox D J, Keith T, AlLaham M A, Peng C Y, Nanayakkara A, Gonzalez C, Challacombe M, Gill P M W, Johnson B, Chen W, Wong M W, Andres J L, Gonzalez C, Head-Gordon M, Replogle E S and Pople J A 2003 *GAUSSIAN 03*, revision A.1 end.; Guassian, Inc.: Pittsburgh, PA

[11] Fujii R, Chen C H, Mizoguchi T and Koyama Y 1998 *Spectrochim. Acta* A **54** 727

[12] Satito S and Tasumi M 1983 *J. Raman Spectrosc.* **14** 310

[13] Yin J H, Gao S Q, Li Z W, Yu Y N, Lu G H and Tian Y J 2004 *J. Raman Spectrosc.* **35** 1042