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Solvent effects on the $S_0 \rightarrow S_2$ absorption spectra of β-carotene*

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Absorption spectra of β-carotene in 31 solvents are measured in ambient conditions. Solvent effects on the 0–0 band energy, the bandwidth, and the transition moment of the $S_0 \rightarrow S_2$ transition are analysed. The discrepancies between published results of the solvent effects on the 0–0 band energy are explained by taking into account microscopic solute-solvent interactions. The contributions of polarity and polarizability of solvents to 0–0 band energy and bandwidth are quantitatively distinguished. The 0–0 transition energy of the S_2 state at the gas phase is predicted to locate between 23000 and 23600 cm^{-1}.

Keywords: solvent effects, absorption spectra, β-carotene
PACC: 3130L, 3320K, 3370J

1. Introduction

Solvent effects on the structural and spectral properties of solute molecules[1,2] or the products of chemical reactions[3] have been extensively investigated by using various theoretical and experimental methods. By employing the cavity model and reaction field theory, Onsager found that the band shifts of absorption spectra in solutions were related to the refractive index and the dielectric properties of solvents.[4] For hydrogen-bond solutes, solvatochromic shifts were also related to the polarity of solvents.[5] In the case of non-polar solutes, a linear relationship was obtained[6] between the absorption band shift and the Bayliss parameter $(n^2-1)/(2n^2+1)$, where n is the refractive index of solvent.

As light-harvesting molecules and photoprotective pigments, carotenoids play an important role in photosynthetic systems.[7] Knowledge of the spectroscopic characteristics of carotenoids in solution is a necessary prerequisite for understanding their functions in complex natural systems,[8,9] so the study of solvent effects on these biological molecules is of great value. The strong visible absorption band of carotenoids is associated with the one-photon allowed $S_0(1^1A_g^-) \rightarrow S_2(1^1B_u^+)$ transition, since the transition from S_0 to the lowest singlet excited state $S_1(2^1A_g^-)$ is one-photon forbidden under the assumption of the C_{2h} symmetry of the molecular backbone.[7] It has been accepted that the dispersive interaction, which is determined by the polarizability of solvent, is the major factor that determines the S_2 state energy.[10] Nagae *et al.* found that the S_2 energy of spheroidene was linearly dependent on the polarizability function $R(n^2)=(n^2-1)/(n^2+2)$ of solvent,[11] and provided a theory to explain the different linear dependences in nonpolar and polar solvents.[12] These investigations indicate that both polarizability and polarity of solvent affect the S_2 energy level. So the solvent polarity function $R(\varepsilon)-R(n^2)=(\varepsilon-1)/(\varepsilon+2)-(n^2-1)/(n^2+2)$, where ε is the dielectric constant of solvent, was used as a solvatochromic scale for the absorption spectra of β-carotene in polar solvents.[13] Other scales, such as $\{a[(\varepsilon-1)/(\varepsilon+1)-(n^2-1)/(n^2+1)]+b(n^2-1)/(n^2+1)\}$[14,15] and $\{aR(n^2)+b[R(\varepsilon)-R(n^2)]\}$[16] were also used to reveal the combined effects of polarity and polarizability. However, knowledge of the physical mechanism of the band shift is still scanty from the microscopic point of view. The 0–0 transition energies at the gas phase obtained from extrapolation in solutions are not consistent in different literature.[12,16]

Classical studies of the solvent effects on absorption spectra of carotenoids focus mainly on the band shift, and much less attention has been paid to the

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bandwidth. A linear relationship between bandwidth and 'excess' redshift in nonalkane solvents was proposed by Torii and Tasumi.[17] The bandwidth was also found to be linear with the polarity function $R(\varepsilon)-R(n^2)$.[13] However, the results of Frank *et al.*[18] suggested that solvent-induced broadening occurred only in carbonyl-containing carotenoids. In addition, conformational disorder was also demonstrated to be a sufficient cause for spectral broadenings.[19] The β-ionone ring interacts with methyl groups of the main conjugated backbone, thereby leading to a certain distribution of ground-state conformers, so the absorption spectra are broadened. This 'distribution of conformers' model has been used to explain the bandwidth of the absorption and fluorescence spectra of a series of apo- and diapocarotenes.[20]

In recent work, we have reported the solvent effects on the Raman[21] and absorption spectra[22] of β-carotene under high pressure. In the present study, we measure the absorption spectra of β-carotene in 31 representative solvents whose polarity and polarizability span a wide range, and systematically reveal the environmental effects on the absorption spectra of carotenoids.

2. Experiment and simulation

β-carotene was purchased from Sigma-Aldrich, stored at −20 °C in the dark, and used without further purification. Absorption spectra of β-carotene solution in a 1 mm thick glass cell were measured on a Varian Cary 4000 spectrophotometer in steps of 1 nm. The absorbance of solvent was subtracted from that of pure solvent in the same cell loaded in the other arm of the spectrophotometer. The fresh solution was used immediately after its preparation to avoid degeneration. All the experiments were performed at room temperature in a darkroom.

The concentrations, estimated from the molar absorptivities[23] and the measured absorption intensities (see Table 1), are lower than 1×10^{-4} mol/L in all the solutions. Li *et al.* found that if the concentration was lower than 50 μg/mL, the fluorescence intensity of lycopene linearly increased with solution concentration increasing,[24,25] indicating that the interaction among lycopene molecules could be ignored when concentration was lower than 1×10^{-4} mol/L. This is also consistent with the results presented by Wang *et al.* who have used the saturated absorption spectra to investigate the 'forbidden' states of carotenoids.[26] For this reason, the solute-solute interactions can be ignored in our experiment, and all the absorption spectra were normalized to their maxima so as to concentrate the attention on the band shift and the band shape. The resolution of absorption spectra are generally not sufficient to allow accurate deconvolution into vibronic components, so the time-domain formula[27,28] was used to simulate the absorption spectra.

In the time-domain formula,[27,28] the absorption cross section $\sigma\left(\omega_{\rm L}\right)$ is given by

$$\sigma\left(\omega_{\rm L}\right)=C\omega_{\rm L}{\rm Re}\int_{0}^{\infty}{\rm d}t\exp\left[{\rm i}\left(\omega_{\rm L}-\omega_0\right)t-\frac{\gamma}{2}t\right]J_{\rm g}\left(t\right)\times\prod_{i=1}^{N}\sigma_i\left(t\right),\tag{1}$$

where

$$J_{\rm g}\left(t\right)=\exp\left\{-\frac{\varDelta^2}{\varLambda^2}\left[\exp\left(-\varLambda t\right)-1+\varLambda t\right]\right\}\tag{2}$$

is the band shape function. $\sigma_i\left(t\right)$ is the absorption kernel of the ith mode, $\omega_{\rm L}$ is the wavenumber of the incident light, ω_0 is the average value of the fluctuating 0–0 band energy, $\varDelta$ and $\varLambda$ are, respectively, the magnitude and the rate of this fluctuation induced by the conformational fluctuations and environmental effects, γ is the total relaxation rate, N is the number of the vibrational modes, and C is a constant. $\varLambda$ and γ can be set as $\varLambda=\gamma=100$ cm^{-1} in the simulation procedure.[22,29] The solvent dependences of the intensity factor (C), the 0–0 band energy (ω_0), and the bandwidth ($\varDelta$) are discussed in the following sections.

3. Results and discussion

3.1. Experiment results

The measured and simulated absorption spectra of β-carotene in two representative solvents are shown in Fig. 1. It is clearly seen that the agreement between the experimental and simulated spectra are satisfactory, and the 0–0 band energy and width can be obtained at a sufficient accuracy. The physical constants of the solvents and simulating parameters are presented in Table 1.

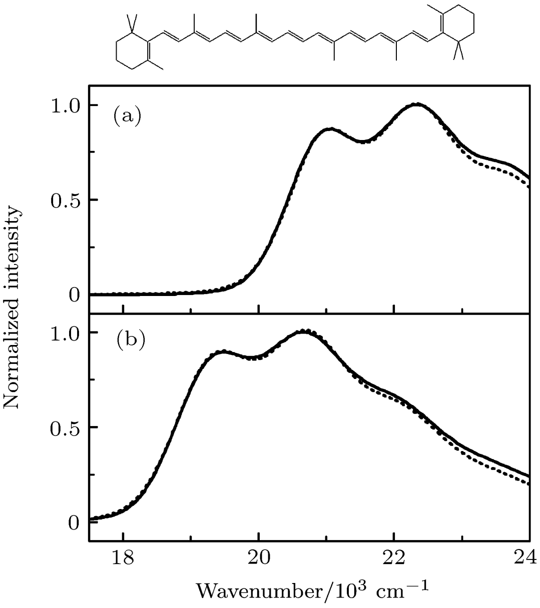

Fig. 1. Molecular structure and the measured (solid lines) and simulated (dot lines) absorption spectra of β-carotene in (a) isopentane and (b) CS_2 solvents.

Table 1. Physical constants of the solvents and simulating parameters of the absorption spectra. $R(n^2) = (n^2 - 1)/(n^2 + 2)$ is the polarizability function, $R(\varepsilon) = (\varepsilon - 1)/(\varepsilon + 2)$ is the polarity function of solvent. ω_0, $\varDelta$, and C are the simulating parameters. Max. is the absorption maximum (i.e. the peak value of the 0–1 band) in a 1 mm thick glass cell.

No.	solvent	$R(n^2)$	$R(\varepsilon)$	ω_0/cm^{-1}	$\varDelta$/cm^{-1}	C	Max.
	nonpolar solvent						
1	Isopentane^{a}	0.217	0.216	20940	530	0.0545	0.23
2	n-pentane^{b}	0.219	0.220	20910	535	0.0540	0.30
3	n-hexane^{b}	0.229	0.229	20800	525	0.0545	0.18
4	n-heptane^{a,b}	0.236	0.236	20760	540	0.0556	0.17
5	n-octane^{a,b}	0.241	0.240	20690	535	0.0550	0.01
6	n-nonane^{a}	0.245	0.244	20680	540	0.0560	0.11
7	n-dodecane^{a}	0.254	0.250	20600	535	0.0550	0.22
8	n-hexadecane^{a,c}	0.261	0.259	20510	545	0.0560	0.06
9	Cyclohexane^{a}	0.256	0.254	20600	540	0.0550	0.52
10	CCl_4^{a}	0.274	0.302	20240	555	0.0575	0.53
11	Benzene^{a}	0.295	0.298	20180	550	0.0570	0.32
12	CS_2^{a}	0.354	0.354	19300	565	0.0600	0.24
	polar solvent						
13	Methanol^{a}	0.203	0.913	20820	565	0.0565	0.03
14	Acetonitrile^{a}	0.212	0.921	20630	580	0.0578	0.07
15	Ethyl ether^{a}	0.216	0.533	20770	550	0.0558	1.19
16	Acetone^{a}	0.220	0.872	20630	570	0.0569	0.42
17	Ethanol^{a}	0.221	0.887	20710	560	0.0570	0.22
18	Ethyl acetate^{a}	0.227	0.626	20680	560	0.0562	0.74
19	2-butanone^{d}	0.231	0.856	20580	560	0.0560	0.30
20	Butan-2-one^{a}	0.231	0.856	20510	560	0.0562	0.92
21	n-butanol^{e}	0.242	0.848	20580	555	0.0566	0.59
22	Tetrahydrofuran^{a}	0.246	0.683	20410	555	0.0565	0.94
23	Dichloromethane^{a}	0.255	0.728	20250	580	0.0580	0.16
24	N,N-dimethylformamide^{a}	0.258	0.923	20220	570	0.0578	0.30
25	Chloroform^{a}	0.267	0.565	20180	575	0.0578	0.26
26	Dimethyl sulfoxide^{a}	0.284	0.938	20150	575	0.0578	0.10
27	Iodoethane^{a}	0.301	0.693	19985	570	0.0585	1.14
28	Benzyl alcohol^{c}	0.314	0.784	19920	570	0.0585	0.23
29	N,N-dimethylaniline^{a}	0.323	0.566	19750	582	0.0597	0.22
30	Aniline^{a}	0.335	0.672	19640	590	0.0605	0.03
31	Quinoline^{d}	0.354	0.733	19620	585	0.0595	0.67

a, b, c, d, and e denote physical constants of this solvent obtained from Refs. [15], [13], [16], [14] and [30], respectively.

According to the explanation given by Myers and Birge,[31] the transition moment decreases with redshift increasing in the absorption spectra of β-carotene. The coefficient C in Eq. (1) is proportional to the square of the transition moment between the ground and excited states.[28] So the fitting parameter C should increase as the redshift of the 0–0 band increases because all the spectra are normalized in our simulation. Figure 2 shows that the value of C does increase, and therefore validates the reliability of the simulation results.

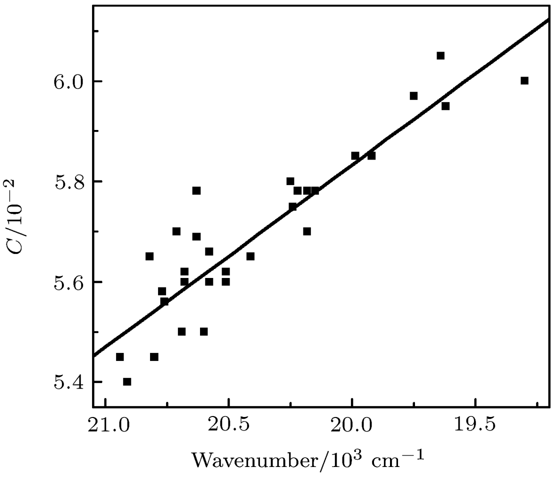

Fig. 2. The values of C against wavenumber of the 0–0 band. The solid line is the fitting line.

3.2. Solvent dependence of 0–0 band energy

It can be seen from Fig. 3(a) that a good linear relationship between the 0–0 band energy and the solvent polarizability function is obtained in 8 alkane solvents, and both the slope and the intercept of line A are consistent with the result given by Chen *et al.*[16] However, a much larger slope and intercept are obtained when the energies in the other four nonpolar solvents are included in the fitting, and line B is obviously inconsistent with the results presented by Chen *et al.*[16] but in good agreement with the results obtained by Nagae *et al.*[12] and Macpherson and Gillbro.[32] These discrepancies in published results can be easily explained by taking into account microscopic solute-solvent interactions, since the short-range interaction has a large effect on the electronic structure of the solute molecule.[33] The dispersive interaction, i.e. the mutual induced polarization of the solute and solvent molecules,[4,30] has been demonstrated to be the major factor that determines the S_2 state energy of the β-carotene in nonpolar solvents.[10] The strength of this dispersive interaction is determined ultimately by the polarizability, the size, and the movement actions of the solvent molecules. The reorientation movement of the relatively large alkane molecules is much slower and weaker than that of the smaller nonpolar molecules (e.g. CCl_4 and CS_2), and the number of the smaller solvent molecules in the solvent shell is much larger than that of alkane molecules, consequently, the dispersive force is stronger in the solvents with small molecular dimensions, and a much larger slope and intercept are obtained[12,32] when the 0–0 band energies in all the 12 nonpolar solvents are fitted. For the results from Chen *et al.*,[16] the active movement and small dimension of supercritical CO_2 molecules visibly enhance the dispersive force and then depress the S_2 state energy. This is the reason why a much smaller slope and intercept are obtained when the 0–0 band energies in supercritical CO_2 and alkane solvents are fitted.[16] It can now be concluded that the intercepts extrapolated from the data in organic solvents (~23600 cm^{-1})[12,32] and supercritical CO_2 (~23000 cm^{-1})[16] are larger and smaller than the real values, respectively. Therefore, we can safely predict that the 0–0 transition energy of β-carotene at the gas phase is between 23000 cm^{-1} and 23600 cm^{-1}.

Figure 3(b) shows the polarizability dependence of the 0–0 band energy in 19 polar solvents. The slope and the intercept of line C are in reasonably good agreement with the results from Nagae *et al.*[12] and Macpherson and Gillbro.[32] It has been revealed that, besides the dispersive interaction, the solvent Stark effect induced by the permanent dipole moments of the solvent can result in further redshift of the absorption spectra.[30] This effect can be identified by the fact that the 0–0 band shifts towards red wavelength visibly in polar solvents compared with those in alkane solvents as shown in Figs. 3(a) and 3(b). The orientational variation of supercritical CHF_3 is too rapid to produce an effective induced-dipole effect on β-carotene molecules, thus the solvent Stark effect can be ignored and the 0–0 band energies are the same as those in supercritical CO_2.[16] The absence of the solvent Stark effect reduces the magnitude of the redshift in supercritical CHF_3, and therefore a larger slope and intercept are obtained when the 0–0 band energies in polar solvents and supercritical CHF_3 are fitted.[16]

Figure 3(c) shows the fitting result of dual linear regression by using the solvatochromic scale $\{a + bR(n^2) + c[R(\varepsilon) - R(n^2)]\}$, where the second and third terms denote the contributions from polarizability and pure polarity, respectively. The parameters of line D are in good agreement with the results presented by Chen *et al.*,[16] and the large value of b/c (30.7) indicates that the band shift depends dominantly on the polarizability of solvent.

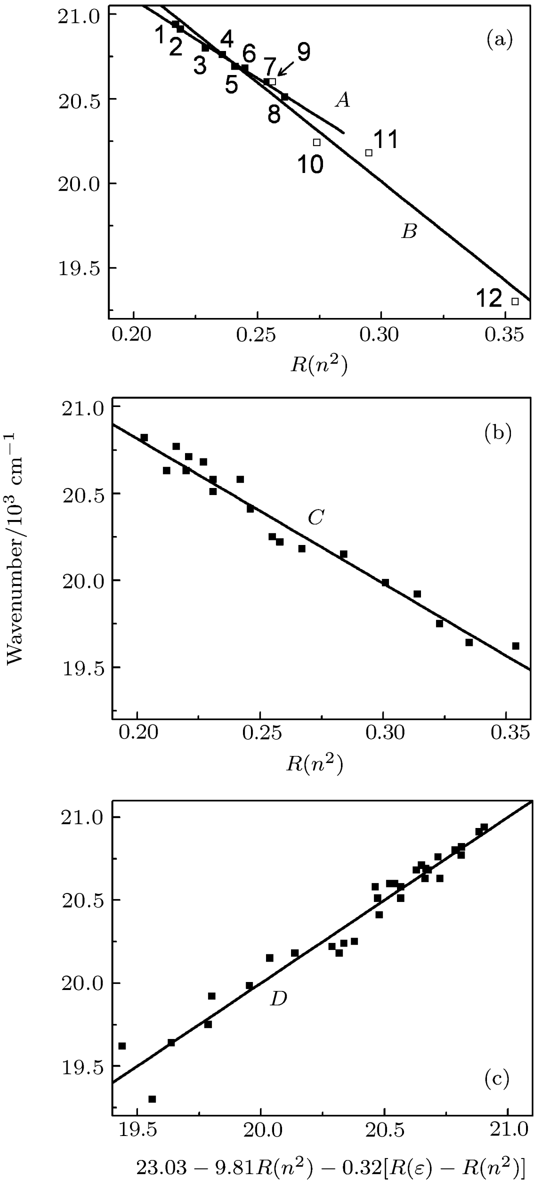

Fig. 3. The 0–0 band energies of absorption spectra of β-carotene against the polarizability function $(R(n^2))$ of (a) nonpolar and (b) polar solvents, and the solvatochromic scale $\{a + bR(n^2) + c[R(\varepsilon) - R(n^2)]\}$ of (c) both nonpolar and polar solvents. The solvents numbered from 1–12 in panel (a) are the same as those in Table 1. The fitting results are as follows: 8 alkane solvents (line A), $(22950 \pm 80) - (9320 \pm 340)R(n^2)$; 12 nonpolar solvents (line B), $(23530 \pm 130) - (11720 \pm 510)R(n^2)$; 19 polar solvents (line C), $(22480 \pm 100) - (8330 \pm 380)R(n^2)$; and all the 31 solvents (line D), $(23030 \pm 110) - (9810 \pm 400)R(n^2) - (320 \pm 60)[R(\varepsilon) - R(n^2)]$.

3.3. Solvent dependence of 0–0 bandwidth

It can be seen from Fig. 4(a) that the bandwidth increases with polarizability increasing and becomes broader in polar solvent than in nonpolar solvent. The bandwidth implies the extent of 0–0 transition energy deviating from the average frequency[27,28] and reflects the environmental effects and the conformational fluctuations of solute molecules. When solvent polarizability increases, the reaction field[4] and the solvent reorganization energy increase due to the larger fluctuation of solvent–solute interactions,[34] so the solvent broadening of the absorption spectrum increases with polarizability increasing. The 'distribution of conformers' model[19,20] can be used to explain the further broadening in polar solvent. The dipole-dipole interactions between the permanent dipole of solvent and the transition dipole of solute molecules

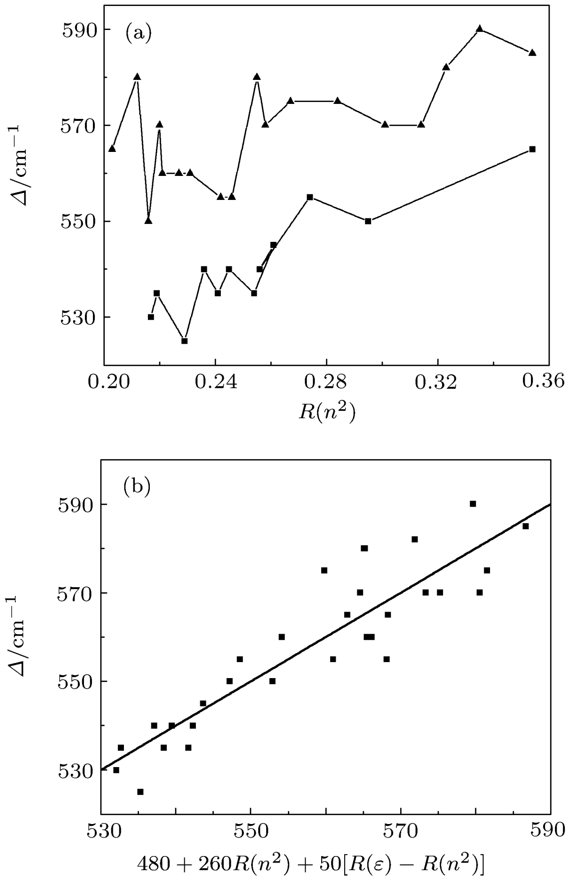

Fig. 4. The values of 0–0 bandwidth ($\varDelta$) of absorption spectra of β-carotene in nonpolar (■) and polar (▲) solvents against (a) the polarizability function $R(n^2)$ and (b) the solvatochromic scale $\{a + bR(n^2) + c[R(\varepsilon) - R(n^2)]\}$. The linear regression formula in panel (b) is $(480 \pm 10) + (260 \pm 30)R(n^2) + (50 \pm 10)[R(\varepsilon) - R(n^2)]$.

facilitate the fluctuations of ground-state conformations along low-frequency molecular vibrational coordinates, thereby broadening the absorption spectrum. Figure 4(a) indicates that both polarizability and polarity affect the 0–0 bandwidth, so the data are also fitted with dual linear regression by using the solvatochromic scale $\{a + bR(n^2) + c[R(\varepsilon) - R(n^2)]\}$ as shown in Fig. 4(b). The small value of b/c (5.2) suggests that the effect of polarity on the bandwidth is much larger than that on the 0–0 band energy of the absorption spectra of β-carotene.

4. Conclusions

The absorption spectra of β-carotene in 31 solvents are measured under normal pressure at room temperature. The transition moment of the $S_0 \rightarrow S_2$ transition decreases gradually with the increase of the redshift of the spectra. The 0–0 band energy depends dominantly on the polarizability of solvent. The bandwidth is relevant to both the environmental effects and the conformational fluctuations of the solute molecule, and the contribution of the polarity of solvents to the 0–0 bandwidth is much larger than to the energy. The inconsistencies in the solvent effect among published results can be explained by taking into account microscopic solute-solvent interactions. It can be predicted from our analyses that the 0–0 transition energy of β-carotene at the gas phase is between 23000 cm^{-1} and 23600 cm^{-1}. This value can provide an important reference for some theoretical investigations, in which the energies of excited states at gas phase are important parameters.

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