

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/5475592>

# Effect of solvent on absorption spectra of all-trans- B -carotene under high pressure

ARTICLE in THE JOURNAL OF CHEMICAL PHYSICS · APRIL 2008

Impact Factor: 2.95 · DOI: 10.1063/1.2841022 · Source: PubMed

CITATIONS

9

READS

74

9 AUTHORS, INCLUDING:



Weilong Liu

Harbin Institute of Technology

53 PUBLICATIONS 248 CITATIONS

SEE PROFILE



Wenzhi Wu

Heilongjiang University

22 PUBLICATIONS 117 CITATIONS

SEE PROFILE



Aihua Li

Xiamen University

44 PUBLICATIONS 442 CITATIONS

SEE PROFILE



Yanqiang Yang

Harbin Institute of Technology

121 PUBLICATIONS 888 CITATIONS

SEE PROFILE

# Effect of solvent on absorption spectra of *all-trans*- $\beta$ -carotene under high pressure

W. L. Liu,<sup>1,a)</sup> Z. R. Zheng,<sup>1,b)</sup> Z. F. Dai,<sup>2</sup> Z. G. Liu,<sup>1</sup> R. B. Zhu,<sup>1</sup> W. Z. Wu,<sup>1</sup> A. H. Li,<sup>1</sup> Y. Q. Yang,<sup>1</sup> and W. H. Su<sup>1,3</sup>

<sup>1</sup>Center for Condensed Matter Science and Technology, Harbin Institute of Technology, Harbin 150001, People's Republic of China

<sup>2</sup>Nanobiotechnology and Biosensor Lab, Bio-X Center, Harbin Institute of Technology, Harbin 150001, People's Republic of China

<sup>3</sup>Department of Physics, Ji Lin University, Changchun 130023, People's Republic of China

(Received 4 September 2007; accepted 15 January 2008; published online 24 March 2008)

The absorption spectra of *all-trans*- $\beta$ -carotene in *n*-hexane and carbon disulfide (CS<sub>2</sub>) solutions are measured under high pressure at ambient temperature. The common redshift and broadening in the spectra are observed. Simulation of the absorption spectra was performed by using the time-domain formula of the stochastic model. The pressure dependence of the 0-0 band wavenumber is in agreement with the Bayliss theory at pressure higher than 0.2 GPa. The deviation of the linearity at lower pressure is ascribed to the reorientation of the solvent molecules. Both the redshift and broadening are stronger in CS<sub>2</sub> than that in *n*-hexane because of the more sensitive pressure dependence of dispersive interactions in CS<sub>2</sub> solution. The effect of pressure on the transition moment is explained with the aid of a simple model involving the relative dimension, location, and orientation of the solute and solvent molecules. The implication of these results for light-harvesting functions of carotenoids in photosynthesis is also discussed. © 2008 American Institute of Physics. [DOI: 10.1063/1.2841022]

## I. INTRODUCTION

The shift of visible and ultraviolet electronic absorption spectra of chromophore in solution from their position in the gas state is called solvatochromic effect.<sup>1</sup> As an important means of understanding intermolecular interactions in solutions, solvatochromic effect can also provide a powerful probe for the study of complex systems.<sup>2</sup> This effect may be classified as *positive* or *negative*, depending on whether they promote a redshift or a blueshift, respectively. Redshifts are called *positive* solvatochromic effects because they are more common.<sup>1</sup> In the case of nonpolar solutes, solvent molecules generate reaction field by responding to the transition dipole of the solute molecule; the linear relationship (Bayliss relation) between the redshift of the absorption band and the Bayliss parameter (BP)  $(n^2 - 1)/(2n^2 + 1)$  is obtained,<sup>3</sup> where *n* is the refractive index of the solvent.

The study of the high-pressure effect on the electronic states of organic and biochemical molecules has a long history. The use of high pressure allows a wide range of the BP at room temperature in a single solvent and therefore can be considered as an alternate way of describing the change in interactions of a molecule with its environment. In addition, the application of hydrostatic pressure can also amplify some intramolecular and intermolecular interactions to make them easier to be investigated.<sup>4,5</sup> Generally speaking, pressure brings two effects on molecular electronic spectra:<sup>6,7</sup> (a) A

pressure dependence of the absorption and luminescence peak positions and (b) a broadening of these peaks. There is usually a shift toward lower energies with the position described by the quadratic function of pressure. Recently, Renge performed a series of nice works on the influence of pressure and temperature on optical impurity spectra in polymer glasses.<sup>8</sup> Inhomogeneous band shapes and the frequency-dependent thermal and baric line shifts were rationalized with the aid of a pair of two-body Lennard-Jones potentials.<sup>9</sup>

Carotenoids and chlorophylls are the most abundant pigments found in nature. As light-harvesting molecules and photoprotective pigments, carotenoids play an important role in photosynthetic systems.<sup>10</sup> Solvatochromic effect of  $\beta$ -carotene, the prototype for many naturally occurring carotenoids, has been extensively studied by various experimental and theoretical methods. Andersson *et al.* measured the absorption spectral shifts in various solvents and concluded that the major factor which determines the energy of the *S*<sub>2</sub> state relative to that of the ground state is the dispersive interactions of the carotenoids with the surrounding molecules.<sup>2</sup> Kuki *et al.* found a systematic difference about the shifts of the *S*<sub>0</sub>→*S*<sub>2</sub> absorption of spheroidene between nonpolar and polar solvents<sup>11</sup> and provided a complete theory for the spectral shifts, which was also applicable for  $\beta$ -carotene.<sup>12</sup> Another improved model was proposed to explain the “excess” redshifts (from the Bayliss relation in alkane solutions) of the absorption spectra in both nonpolar and polar solvents.<sup>13</sup> The relationship between the excess redshifts and the 0-0 bandwidths was revealed.<sup>13</sup> Temperature can also produce obvious influence on the line shapes of

<sup>a)</sup>Electronic mail: liuwl\_163@163.com.

<sup>b)</sup>Author to whom correspondence should be addressed.

Tel.: +86-451-86418440. FAX: +86-451-86418440. Electronic mail: rzzheng@hit.edu.cn.

the absorption spectra. Detailed analyses of the temperature effect can provide important information about the solvent-solute interactions,<sup>14</sup> the mechanism of internal conversion and intramolecular vibrational redistribution,<sup>15</sup> and solvent dynamics.<sup>16</sup>

A general knowledge about the properties of carotenoids in solution is the prerequisite for understanding their functions in more complex natural and artificial systems. The obvious difference of solvent environment and native living organisms justifies the need for a reasonable conjunction between the photochemical properties of carotenoids in those two matrices. The absorption maxima of a single carotenoid species can be shifted over a wide range by highly specific interactions with proteins.<sup>11</sup> The comparability of this shift with high-pressure absorption makes it possible to mimic the effect of native environment on carotenoids.<sup>17</sup>

The spectral properties of solvated carotenoids have been extensively investigated at ambient pressure;<sup>10</sup> however, to the best of our knowledge, only a few studies have been done under high pressure. Ho *et al.* measured the absorption spectra<sup>17</sup> and resonance Raman excitation profile<sup>18</sup> of  $\beta$ -carotene in the pressure range up to 7.0 GPa. A multi-mode model was proposed to analyze the data. Ellervee and Freiberg investigated the pressure effect on the absorption spectrum of  $\beta$ -carotene and lycopene.<sup>19</sup> The absorption band origin was found to be nonlinearly dependent on the solvent polarizability, especially in the lower pressure range.<sup>19</sup>

Since the protein environment is thought to be nonpolar,<sup>11</sup> it is appropriate to perform the high-pressure spectroscopic study in nonpolar solvent. We have investigated the high-pressure Raman spectra of *all-trans*- $\beta$ -carotene (referred to hereafter as  $\beta$ -carotene) in *n*-hexane and CS<sub>2</sub>.<sup>20</sup> In this paper, the high-pressure absorption spectra of  $\beta$ -carotene in these two solvents are reported. Some significant conclusions were obtained when comparing the effect of solvent on the spectra.

## II. EXPERIMENT

The  $\beta$ -carotene was purchased from Sigma-Aldrich, stored at  $-20^\circ\text{C}$  in the dark and used without further purification. The amount of 15-*cis* isomer was negligible because almost no absorption band was observed around 340 nm before the measurements.<sup>21</sup> The  $\beta$ -carotene was dissolved in *n*-hexane (high performance liquid chromatography grade) or CS<sub>2</sub> (analytical grade). The concentrations were  $\sim 2 \times 10^{-4}$  and  $\sim 8 \times 10^{-4} \text{ M}$  for *n*-hexane and CS<sub>2</sub> solutions, respectively. In all the experiments, fresh solution was used immediately after its preparation to avoid degeneration. No crystal was precipitated out during the measurements.

Quasihydrostatic pressure was applied to the sample using a conventional diamond anvil cell (DAC).<sup>22</sup> Two diamonds with 0.5 mm culet faces were used. The gasket was made of stainless steel with an initial thickness of 0.3 mm and had a hole with an initial diameter of 0.25 mm. The pressure inside the cell was determined by observing the shift of fluorescence ( $R_1$  line) from a small ruby contained within the sample cell.<sup>23</sup>

The absorption spectra measurements were carried out

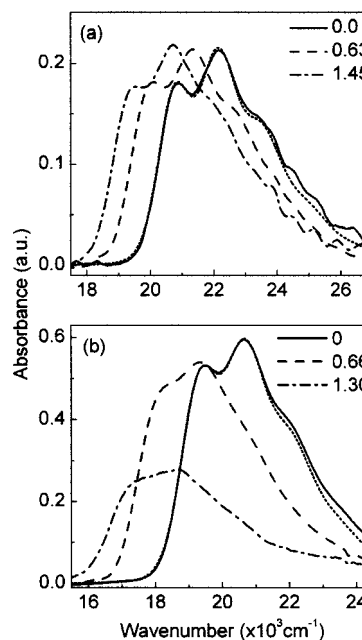


FIG. 1. Pressure dependence of absorption spectra of  $\beta$ -carotene in (a) *n*-hexane at 0, 0.63, and 1.45 GPa, and (b) CS<sub>2</sub> at 0, 0.66, and 1.30 GPa. The short-dot lines are the simulated spectra at ambient pressure.

on a Varian Cary 4000 spectrophotometer with 1 nm step. The DAC was fixed in the spectrophotometer by a home-made holder. The absorption spectrum was corrected in each case for the background absorption of the diamonds and other optical components. Ruby fluorescence was excited by a focused neon-helium laser (632.8 nm) with the power less than 1 mW and was collected by a fiber and coupled to a 50 cm spectrometer (BRUKER Chromex 500 is/sm) equipped with a thermoelectrically cooled charge-coupled device (Andor DU440). The spectrum resolution of fluorescence is 0.025 nm, so the error of pressure calibration is  $\pm 0.03$  GPa. All the experiments were performed at room temperature in a darkroom.

## III. SIMULATION OF THE ABSORPTION SPECTRA

The solidified pressures measured in our experiment are, respectively,  $\sim 1.45$  and  $\sim 1.3$  GPa for *n*-hexane and CS<sub>2</sub> solutions, which are in good agreement with literature.<sup>24,25</sup> Several representative absorption spectra in *n*-hexane and CS<sub>2</sub> solutions are shown in Fig. 1. Besides the broadening of the vibronic bands in both solutions, the absorption intensity increases (decreases) gradually in *n*-hexane (CS<sub>2</sub>) solution with increasing pressure. The absorption intensity in CS<sub>2</sub> exhibits an even more decrease after solidification and finally disappears, although the solid is transparent.

Simulation of the absorption spectra was performed by using the time-domain formula derived by Yan and co-workers.<sup>26,27</sup> In their formulation, the absorption cross section  $\sigma(\omega_L)$  is given by

TABLE I. Ground ( $\omega_i''$ ) and excited ( $\omega_i'$ ) state vibrational frequencies and dimensionless displacements  $D_i$  used to calculate the absorption spectra of  $\beta$ -carotene in  $n$ -hexane ( $D_i^a$ ) and CS<sub>2</sub> ( $D_i^b$ ) solutions.

Mode	$\omega_i''$	$\omega_i'$	$D_i^a$	$D_i^b$
1	1525	1580	1.10	1.04
2	1155	1220	0.95	0.95
3	1005	1005	0.65	0.65

$$\sigma(\omega_L) = C\omega_L \operatorname{Re} \int_0^\infty dt \times \exp[i(\omega_L - \omega_0)t - t\gamma/2] J_g(t) \prod_{i=1}^n \sigma_i(t), \quad (1)$$

where

$$J_g(t) = \exp\{-[\exp(-\Lambda t) - 1 + \Lambda t]\Delta^2/\Lambda^2\} \quad (2)$$

is the band-shape function. This Gauss function indicates a stochastic model in describing the modulation of the 0-0 wavenumber due to solvent-solute interactions.  $\sigma_i(t)$  is the absorption kernel of the  $i$ th mode,  $\omega_L$  is the wavenumber of the incident light,  $\omega_0$  is the average of the fluctuating 0-0 wavenumber,  $\Delta$  and  $\Lambda$  are the magnitude and the rate of this fluctuation, respectively,  $\gamma$  is the relaxation rate,  $N$  is the number of the vibrational modes, and  $C$  is a constant. For  $\beta$ -carotene solution,  $\Lambda$  and  $\gamma$  can be set as  $\Lambda = \gamma = 100 \text{ cm}^{-1}$ .<sup>14</sup>

The explicit form of the absorption kernel  $\sigma_i(t)$  at temperature  $T$  is given by<sup>14</sup>

$$\sigma_i(t) = [\Psi_{Ti}(t)]^{-1/2} \exp[D_i^2 f_{Ti}(t)], \quad (3)$$

with

$$\Psi_{Ti}(t) = (\omega_i'' C_{+i} A_{-i} + \omega_i' C_{-i} A_{+i})(\omega_i' C_{+i} A_{-i} + \omega_i'' C_{-i} A_{+i})/4\omega_i' \omega_i'', \quad (4)$$

$$f_{Ti}(t) = -(\omega_i'' C_{-i} A_{-i})/(\omega_i' C_{+i} A_{-i} + \omega_i' C_{-i} A_{+i}), \quad (5)$$

where

$$C_{\pm i} = 1 \pm \exp(-i\omega_i' t), \quad (6)$$

$$A_{\pm i} = (\bar{n}_i + 1) \pm \bar{n}_i \exp(i\omega_i'' t), \quad (7)$$

$$\bar{n}_i = [\exp(\omega_i''/kT) - 1]^{-1}. \quad (8)$$

In these equations,  $\omega_i'$  and  $\omega_i''$  denote, respectively, the  $i$ th vibrational frequencies in the excited and ground states, and  $D_i$  is the dimensionless displacement between the equilibrium configurations of the two electronic states along the  $i$ th mode. All the broadening is summed up to  $\Delta$ , which is the fluctuation of 0-0 wavenumber caused by the interaction of the solute and solvent molecules.  $\Delta$  defined in this way means that the absorption spectrum is inhomogeneously broadened.

Ground and excited state vibrational frequencies and dimensionless displacements presented in Table I were determined by referring to the literature<sup>14,28</sup> and examining the fitted results (see Fig. 1) for our experimental data at ambient

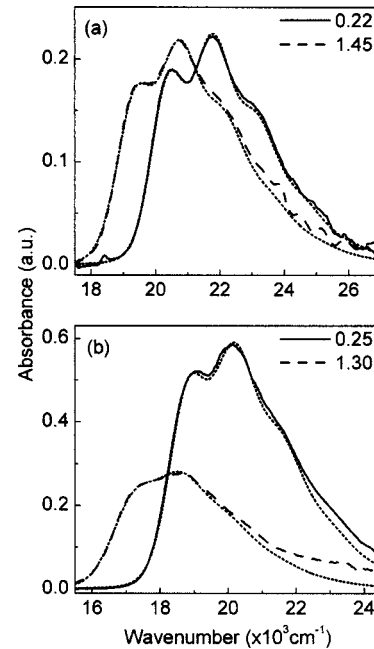


FIG. 2. Absorption spectra of  $\beta$ -carotene in (a)  $n$ -hexane at 0.22 and 1.45 GPa, and (b) CS<sub>2</sub> at 0.25 and 1.30 GPa. Short-dot lines are calculated spectra at each pressure.

pressure. The small difference of  $D_1$  in Table I can be assigned to the solvent effect on the C=C stretching mode.<sup>20</sup> We performed simulation of the spectra at all the measured pressure points and obtained the similar degree of fitting, as shown in Fig. 2. In calculating the spectra at high pressures, only  $\Delta$ ,  $\omega_0$ , and  $C$  are changed. Since the small change in the structure of  $\beta$ -carotene under high pressure does not play any role in the absorption spectra,<sup>20</sup> we made only small corrections (within 3%) on  $D_i$  to obtain a good fit for each spectrum, and these values can also be regarded as essentially the same for all the spectra.<sup>13</sup> The various pressure dependences of the fitted parameters  $\Delta$ ,  $\omega_0$ , and  $C$  are analyzed in detail in the following parts.

## IV. RESULTS AND DISCUSSIONS

### A. Pressure dependence of the 0-0 band wavenumber

The Bayliss theory<sup>3</sup> predicted that the change of transition energy  $\Delta\omega$  is in proportion with BP,

$$\Delta\omega = k \frac{n^2 - 1}{2n^2 + 1} = kBP, \quad (9)$$

where  $k$  is related to the transition moment and the volume of the solute cavity.

The refractive index of the solvent was determined by the Lorentz-Lorentz relation

$$\frac{n^2 - 1}{n^2 + 2} = b\rho, \quad (10)$$

where  $\rho$  is the density and  $b$  is a constant that can be calculated by the refractive index and density at ambient pressure to be 0.3468 and 0.2862 for  $n$ -hexane and CS<sub>2</sub>, respectively. The density of solvent under high pressure can be determined by the Tait equation. The parameters in the Tait equation

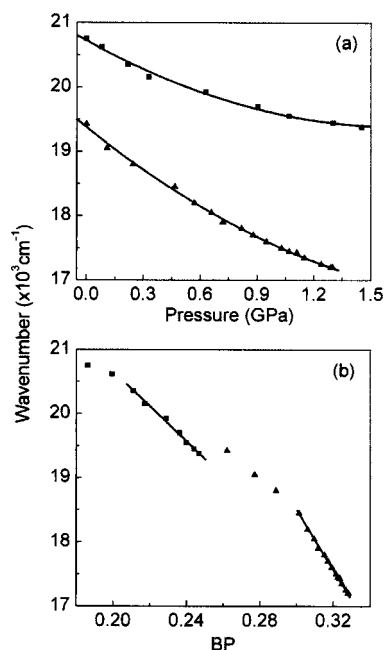


FIG. 3. The 0-0 band wavenumber vs (a) pressure and (b) BP in *n*-hexane (■) and CS<sub>2</sub> (▲) solutions. The solid lines are (a) quadratic polynomial and (b) linear fitting of the data points. The fitted parameters are shown in Table II.

tion for *n*-hexane were provided by Cibulka and Hnědkovský.<sup>29</sup> We fitted the compression data of Danforth<sup>30</sup> to the Tait equation to get the pressure dependence of density for CS<sub>2</sub>. The redshifts of 0-0 bands are plotted against pressure and BP in Fig. 3. The functions and parameters for fitting the data points are presented in Table II.

The pressure dependence of 0-0 band wavenumbers shown in Fig. 3(a) agrees on a common result, that is to say, the 0-0 band shifts toward lower energy and this shift tends to saturate with the pressure increasing. However, Fig. 3(b) shows an interesting deviation from the linear dependence on BP in the pressure range lower than 0.2 GPa. The similar result in *n*-hexane solution has also been obtained by Ellervee and Freiberg.<sup>19</sup> In order to explain the abnormal deviation, the original dielectric theories<sup>3</sup> of solvatochromic effect must be re-examined. An essential assumption of these theories is that both the solute and solvent molecules keep the random orientations and fixed positions during the rapid “vertical” Franck–Condon absorption. However, the relative orientation and position of the solute and solvent molecules are not identical at different pressures. The theoretical and experimental results about liquid CS<sub>2</sub> under high pressure<sup>31,32</sup> need us to describe the physical process as follows. At first, the relative orientation of the adjacent molecules are adjusted<sup>32</sup> and the parallel configuration is favorable.<sup>31</sup> Then, with increasing pressure, the intermolecu-

lar distance decreases while holding the relatively small changes in orientation of the adjacent molecules.<sup>32</sup> This physical picture can also hold true for liquid *n*-hexane, although the relative orientation of the adjacent molecules is unnecessarily parallel. Therefore, the deviation of linearity in the lower pressure range can be reasonably assigned to the reorientation of the solvent molecules at different pressure points. The linearity relation of the 0-0 band energy and BP achieved by Ho *et al.*<sup>17</sup> can be ascribed to the wide pressure range (0–6 GPa), which conceals the nonlinearity in the lower pressure region.

The increased BP of the solvent is generally thought responsible for the redshift of absorption spectra under high pressure; however, the diverse BP dependences in different solvents<sup>6</sup> have not been explained. In fact, the increase of BP roots in the increased density. Theoretical calculation has reported that<sup>33</sup> as the density of the solvent increases, the amount of solvent molecules surrounding the solute increases, and the dispersive force and therefore, the original redshift of the absorption are enhanced. The increased density in the lower pressure region results mainly from the reorientation of the solvent molecules, and the amount of solvent molecules surrounding the solute does not change visibly, so the redshifting rate of 0-0 band is much smaller in this pressure range in both solutions. Since the density of CS<sub>2</sub> increases more rapidly than that of *n*-hexane with increasing pressure,<sup>29,30</sup> the amount of solvent molecules in the first solvation layer, which is responsible for most part of the dispersive force, increases more rapidly and leads to a larger slope for the linear part of CS<sub>2</sub> solution in Fig. 3(b). We estimated the slope of  $\Delta\nu$  vs BP in Ref. 17 to be  $-27\,000\text{ cm}^{-1}$ , which is in good agreement with the slope of the linear part in *n*-hexane solution ( $-27\,276\text{ cm}^{-1}$ ). This consistency can be ascribed to the similar pressure dependence of solvent densities in the two experiments (1:1 mixture of *n*-pentane and isopentane in Ref. 17 and *n*-hexane in our experiment).

It is well known that the density of solvent depends on both pressure and temperature. Torii and Tasumi investigated the temperature effect on  $\beta$ -carotene absorption spectra in isopentane at ambient pressure.<sup>14</sup> The linear dependence of 0-0 wavenumber on BP was obtained, but the slope ( $19\,000\text{ cm}^{-1}$ ) is much smaller than the value ( $27\,000\text{ cm}^{-1}$ ) obtained at room temperature under high pressure.<sup>17</sup> The similar differences of temperature and pressure effects on the fluorescence yields of 1,6-diphenyl-1,3,5-hexatriene have also been observed.<sup>7</sup> In fact, the dispersive force depends not only on the amount of solvent molecules in the first solvation layer but also on the extent of the solvent motion.<sup>16</sup> Although the molecular amount in the first solvation layer increases at low temperature, the inactive solvent motion weakens this effect and leads to a gentler BP dependence of 0-0 wavenumbers than that under high pressure at ambient temperature.

TABLE II. Fitted parameters for the pressure ( $A+B\cdot P+C\cdot P^2$ ) and BP ( $I+S\cdot BP$ ) dependence of the 0-0 band wavenumber in Fig. 3.

Solvent	$A\text{ (cm}^{-1}\text{)}$	$B\text{ (cm}^{-1}\text{ GPa}^{-1}\text{)}$	$C\text{ (cm}^{-1}\text{ GPa}^{-2}\text{)}$	$I\text{ (cm}^{-1}\text{)}$	$S\text{ (cm}^{-1}\text{)}$
<i>n</i> -hexane	20721	-1620	490	26 118	-27 276
CS <sub>2</sub>	19375	-2348	512	32 646	-47 123

## B. Pressure dependence of the 0-0 bandwidth

It has been concluded<sup>14,20</sup> that the environmental effect (temperature or pressure), but not the structural change, is responsible for the spectral properties of a given carotenoid



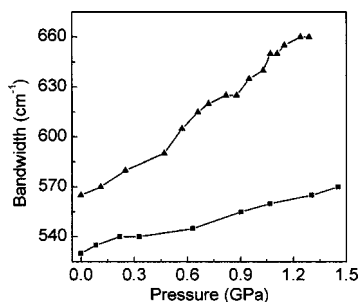


FIG. 4. Effect of pressure on the 0-0 bandwidth ( $\Delta$ ) in *n*-hexane (■) and CS<sub>2</sub> (▲) solutions.

species. Solvent<sup>34</sup> and temperature<sup>14</sup> effects have been used to reveal the environmental influence on absorption spectra of  $\beta$ -carotene. Both results confirm that the 0-0 bandwidth is related to the intermolecular interaction between  $\beta$ -carotene and solvent molecules. It can be seen from the pressure dependence of 0-0 bandwidth ( $\Delta$ ) shown in Fig. 4 that the values of  $\Delta$  rise in both solutions. However,  $\Delta$  rises more rapidly in CS<sub>2</sub> than that in *n*-hexane, which means that the fluctuation of intermolecular interactions varies more significantly with pressure in CS<sub>2</sub>. In addition, the small values of  $\kappa = \Lambda/\Delta$  (0.1–0.2) confirms our postulate that the high-pressure absorption spectrum of  $\beta$ -carotene is inhomogeneously broadened for the most part.<sup>16</sup>

### C. Pressure dependence of the transition moment

The pressure dependent feature of the parameter  $C$  in Eq. (1) is also found. On the whole, although fluctuating within a small range, it undergoes a visible increase (decrease) in *n*-hexane (CS<sub>2</sub>) solution and rapidly vanishes in CS<sub>2</sub> solution after solidification. If  $C$  at ambient pressure is set to unity, the relative values of  $C$  at different pressure are shown in Fig. 5. Since the constant  $C$  is proportional to the square of transition moment ( $\mu^2$ ) between the ground and excited states,<sup>27,35</sup> we can safely attribute the change of  $C$  to the variation of transition moment.

The effect of solvent on oscillator strength for the absorption transition of  $\beta$ -carotene at ambient pressure has been investigated by Myers and Birge by using the first-order perturbation theory.<sup>36</sup> In their model, the net transition dipole moment between the perturbed ground and excited states is a vector sum of the solute molecular dipole moment (source dipole) and the induced dipoles of all the solvent molecules.

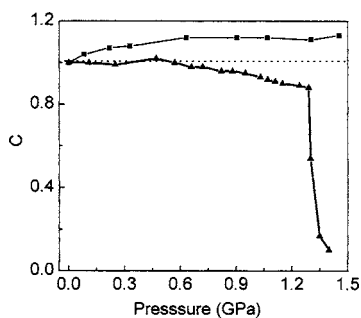


FIG. 5. Effect of pressure on the relative value of  $C$  in *n*-hexane (■) and CS<sub>2</sub> (▲) solutions. The dash line at  $C=1$  is plotted to guide the eyes.

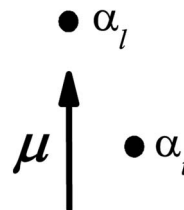


FIG. 6. The two-dimensional representation of the effective-solvent model. For the detailed interpretation, see the text.

Liver *et al.* found that the first-order quantum-mechanical perturbation theory of the solvent effect on molecular transition dipole moment is equivalent to the classical electrostatic approach.<sup>37</sup> Vallée *et al.* further explored the previous approach and provides a full microscopic interpretation.<sup>38</sup> The effect of microscopic structure (relative dimension, orientation, and position) of the environmental molecules around the probe molecule on the molecular transition dipole moment was illustrated by the classical electrostatic approach. The different pressure dependences of the molecular oscillator strengths, as shown in Fig. 5, need us to take the influence of microscopic environment into account.

Renge's idea of simplifying the system to an effective two-body interaction<sup>9</sup> is used in our model. Since the transversal and longitudinal locations of the environmental molecule can bring about different effects on the total transition dipole moment of the system,<sup>38</sup> we propose a model involving two nonpolar effective solvent molecules located transversally and longitudinally with respect to the dipole axis of the  $\beta$ -carotene monomer. Figure 6 shows the two-dimensional sketch map of our model, where  $\mu$  is the dipole moment of the free solute molecule; the effective solvent molecules are represented by two spherical cells with identical volume ( $V$ ). The transversal and longitudinal effective solvent molecule represents all the solvent molecules located at the flank and the two ends of the  $\beta$ -carotene molecule, respectively. The probabilities that the solvent molecules appear at the flank and the end of the  $\beta$ -carotene molecule are not identical, so the induced-dipole moments of the two effective solvent molecules are different. This difference is ascribed to the difference of the polarizabilities ( $\alpha_t$  and  $\alpha_l$ ) for the transversal and longitudinal effective solvent molecules in the present model. The induced-dipole–induced-dipole interaction between the effective solvent molecules is ignored. The electric fields induced by  $\mu$  at the transversal and longitudinal locations are

$$\mathbf{E}_t = -\mu/4\pi\epsilon_0 r_t^3, \quad (11a)$$

and

$$\mathbf{E}_l = \mu/2\pi\epsilon_0 r_l^3, \quad (11b)$$

where  $r_t$  ( $r_l$ ) is the intermolecular distance between the solute and effective solvent molecules at the transversal (longitudinal) position. The total transition dipole moment of the system can be represented as

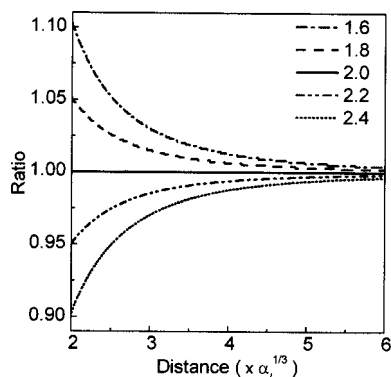


FIG. 7. The distance dependence of the ratio  $(\mu_{\text{tot}}/\mu)^2$  calculated by Eq. (13) for different values (1.6, 1.8, 2.0, 2.2, and 2.4) of  $\alpha_t/\alpha_l$ . The intermolecular distance is expressed in units of  $\alpha_l^{1/3}$  in the Gauss scale.

$$\mu_{\text{tot}} = \mu + \alpha_t \mathbf{E}_t + \alpha_l \mathbf{E}_l = \mu - \alpha_t \mu / 4\pi\epsilon_0 r_t^3 + \alpha_l \mu / 2\pi\epsilon_0 r_l^3. \quad (12)$$

Since the intermolecular distance between the solute and effective solvent molecule is determined by the isotropic van der Waals force, we can reasonably confirm that  $r_t = r_l = r$ . The total transition moment can now be written as

$$\mu_{\text{tot}} = \mu[1 - (\alpha_t - 2\alpha_l)/4\pi\epsilon_0 r^3]. \quad (13)$$

The volumes ( $V$ ) of the effective solvent molecules are different for various solvents, so the relative probability that the solvent molecules appear at the transversal and longitudinal positions is different, and therefore the relative polarizabilities  $\alpha_t/\alpha_l$  are also different for diverse solvents. Figure 7 presents the distance dependence of  $(\mu_{\text{tot}}/\mu)^2$  for several representative values of  $\alpha_t/\alpha_l$ . For a given solvent species with  $\alpha_t/\alpha_l > 2$  ( $\alpha_t/\alpha_l < 2$ ), the total transition moment decreases (increases) with the decreasing intermolecular distance.

This model can reasonably explain the experimental results shown in Fig. 5. The volume of the  $\text{CS}_2$  molecule is very small relative to that of  $\beta$ -carotene, so it is more probable for the solvent molecules to appear at the flank of the  $\beta$ -carotene molecule. This means the polarizability  $\alpha_t$  is much larger than  $\alpha_l$ . Figure 7 shows that if the ratio of  $\alpha_t/\alpha_l$  is larger than 2, the total transition dipole moment is decreased with decreasing intermolecular distance. The consistency between the theoretical model and experimental results indicates that the ratio of  $\alpha_t/\alpha_l$  is larger than 2 for  $\text{CS}_2$ . The condition of  $\alpha_t/\alpha_l < 2$  can be satisfied in  $n$ -hexane solution because of the large volume of this solvent molecule, and therefore the total transition moment increases with the rising pressure.

It is also worth noting that the intensity of the absorption spectra egregiously decreases suddenly in  $\text{CS}_2$  when the solution is solidified and finally disappears. This phenomenon needs us to take the relative orientation of the solute and solvent molecules into account. It has been speculated from the Raman spectra that the transition moments of  $\text{CS}_2$  at the flank of the  $\beta$ -carotene molecule are perpendicular to that of the  $\beta$ -carotene molecular plane in the solid phase.<sup>20</sup> Therefore, we can reasonably come to the conclusion that if the intermolecular distance between the solvent, whose transition moment is perpendicular to that of the solute, and solute

molecule decreases to some certain extent, the oscillator strength for the absorption transition of the solute molecule will be markedly decreased.

## D. Implications for light harvesting in LH2

This investigation may present some implications for understanding the light-harvesting function of carotenoids in photosynthetic systems, especially the peripheral light-harvesting antenna complexes (LH2) of purple bacteria, whose structure have been resolved in great detail.<sup>39</sup> The bacteriochlorophylls B800 and B850 are located at the flank and end of the carotenoid molecule in LH2 and correspond to the transversal and longitudinal effective solvent molecules in our model, respectively. Thus, containing more B850, compared with B800, is favorable for the compact complexes to capture more light energy. This consideration indicates that the disposition of pigments in the LH2 complex is well designed for efficient light harvesting. Furthermore, according to the result, which takes the relative orientation into account, mentioned in the above paragraph, the transition dipole moment of carotenoid in LH2 is decreased due to the existence of B800. It is because that B800 is located at the transversal position and both its  $Q_x$  and  $Q_y$  transition dipoles are approximately perpendicular to that of carotenoid.<sup>40</sup> This may be the reason that the absorption intensity of carotenoids is enhanced in LH2 when B800 is depleted.<sup>41</sup> These results suggest that it may be not accurate enough to conjecture the pigment components of the native complexes merely from the intensity of the steady-state absorption spectrum, especially when the pigments are very close to each other.

## V. CONCLUSIONS

The absorption spectra of  $\beta$ -carotene in  $n$ -hexane and  $\text{CS}_2$  solutions are measured under high pressure and analyzed by using the time-domain formula of the stochastic model. The pressure dependence of the 0-0 band wavenumber can be described by the Bayliss theory at the pressure higher than 0.2 GPa before solidification. The deviation of the linearity in the lower pressure range can be assigned to the reorientation of the solvent molecules. Both the redshift and broadening are stronger in  $\text{CS}_2$  than that in  $n$ -hexane because of the more sensitive pressure dependence of dispersive interactions in  $\text{CS}_2$  solution. The effect of pressure on the transition moment of  $\beta$ -carotene is reviewed with the aid of a simple model, which takes into account the relative dimension, position, and orientation of the solute and solvent molecules. The results of this work indicate that the high-pressure spectroscopy of carotenoids in solutions can provide a novel insight for understanding their photophysics properties in photosynthetic systems.

## ACKNOWLEDGMENTS

We thank Professor Arvi Freiberg for kindly providing some of their research results for reference. We are also indebted to Professor Jian-Ping Zhang and Hai-Fei Zheng for the helpful discussion on the dipolar interactions in LH2 and

the local structure of liquids under high pressure, respectively. This work was supported by the National Natural Science Foundation of China (Grant Nos. 10774034, 60478015, 10674034, and 10504005).

- <sup>1</sup>C. J. Cramer and D. G. Trular, *Chem. Rev. (Washington, D.C.)* **99**, 2161 (1999).
- <sup>2</sup>P. O. Andersson, T. Gillbro, L. Ferguson, and R. J. Cogdell, *Photochem. Photobiol.* **54**, 353 (1991).
- <sup>3</sup>N. S. Bayliss, *J. Chem. Phys.* **18**, 292 (1950).
- <sup>4</sup>A. Ellervee, J. Linnanto, and A. Freiberg, *Chem. Phys. Lett.* **394**, 80 (2004).
- <sup>5</sup>K. Timpmann, A. Ellervee, T. Pullerits, R. Ruus, V. Sundström, and A. Freiberg, *J. Phys. Chem. B* **105**, 8436 (2001).
- <sup>6</sup>B. Y. Okamoto and H. G. Drickamer, *J. Chem. Phys.* **61**, 2870 (1974).
- <sup>7</sup>L. A. Brey, G. B. Schuster, and H. G. Drickamer, *J. Chem. Phys.* **71**, 2765 (1979).
- <sup>8</sup>I. Renge, *J. Phys. Chem. A* **110**, 3533 (2006); **105**, 9094 (2001); **104**, 7452 (2000); **104**, 3869 (2000).
- <sup>9</sup>I. Renge, *J. Phys. Chem. B* **108**, 10596 (2004); *Chem. Phys. Lett.* **405**, 404 (2005); *J. Chem. Phys.* **127**, 034504 (2007).
- <sup>10</sup>T. Polívka and V. Sundström, *Chem. Rev. (Washington, D.C.)* **104**, 2021 (2004).
- <sup>11</sup>M. Kuki, H. Nagae, R. J. Cogdell, K. Shimada, and Y. Koyama, *Photochem. Photobiol.* **59**, 116 (1994).
- <sup>12</sup>H. Nagae, M. Kuki, R. J. Cogdell, and Y. Koyama, *J. Chem. Phys.* **101**, 6750 (1994).
- <sup>13</sup>H. Torii and M. Tasumi, *J. Chem. Phys.* **98**, 3697 (1993).
- <sup>14</sup>H. Torii and M. Tasumi, *J. Phys. Chem.* **94**, 227 (1990).
- <sup>15</sup>S. Akimoto, I. Yamazaki, T. Sakawa, and M. Mimuro, *J. Phys. Chem. A* **106**, 2237 (2002).
- <sup>16</sup>J. A. Burt, X. H. Zhao, and J. L. McHale, *J. Chem. Phys.* **120**, 4344 (2004).
- <sup>17</sup>Z. Z. Ho, T. A. Moore, S. H. Lin, and R. C. Hanson, *J. Chem. Phys.* **74**, 873 (1981).
- <sup>18</sup>Z. Z. Ho, R. C. Hanson, and S. H. Lin, *J. Phys. Chem.* **89**, 1014 (1985).
- <sup>19</sup>A. Ellervee and A. Freiberg, *Diffus. Defect Data, Pt. A* **208–209**, 135 (2002).
- <sup>20</sup>W. L. Liu, Z. R. Zheng, R. B. Zhu, Z. G. Liu, D. P. Xu, H. M. Yu, W. Z. Wu, A. H. Li, Y. Q. Yang, and W. H. Su, *J. Phys. Chem. A* **111**, 10044 (2007).
- <sup>21</sup>Z. D. Pendon, G. N. Gibson, I. van der Hoef, J. Lugtenburg, and H. A. Frank, *J. Phys. Chem. B* **109**, 21172 (2005).
- <sup>22</sup>G. J. Piermarini and S. Block, *Rev. Sci. Instrum.* **46**, 973 (1975).
- <sup>23</sup>H. K. Mao, P. M. Bell, J. V. Shaner, and D. J. Steinberg, *J. Appl. Phys.* **49**, 3276 (1978).
- <sup>24</sup>H. Wang, H. F. Zheng, and Q. Sun, *Appl. Spectrosc.* **59**, 1498 (2005).
- <sup>25</sup>A. Ishizumi, M. Kasami, T. Mishina, S. Yamamoto, and J. Nakahara, *High Press. Res.* **23**, 201 (2003).
- <sup>26</sup>S. Mukamel, S. Abe, Y. J. Yan, and R. Islampour, *J. Phys. Chem.* **89**, 201 (1985).
- <sup>27</sup>Y. J. Yan and S. Mukamel, *J. Chem. Phys.* **85**, 5908 (1986).
- <sup>28</sup>J. Sue and S. Mukamel, *J. Opt. Soc. Am. B* **5**, 1462 (1988).
- <sup>29</sup>I. Cibulka and L. Hnědkovský, *J. Chem. Eng. Data* **41**, 657 (1996).
- <sup>30</sup>W. E. Danforth, Jr., *Phys. Rev.* **38**, 1224 (1931).
- <sup>31</sup>Y. Fujita and S. Ikawa, *J. Chem. Phys.* **103**, 9580 (1995).
- <sup>32</sup>S. Yamamoto, Y. Ishibashi, Y. Inamura, Y. Katayama, T. Mishina, and J. Nakahara, *J. Chem. Phys.* **124**, 144511 (2006).
- <sup>33</sup>M. D. Stephens, J. G. Saven, and J. L. Skinner, *J. Chem. Phys.* **106**, 2129 (1997).
- <sup>34</sup>A. N. Macpherson and T. Gillbro, *J. Phys. Chem. A* **102**, 5049 (1998).
- <sup>35</sup>S. Mukamel, *J. Chem. Phys.* **82**, 5398 (1985).
- <sup>36</sup>A. B. Myers and R. R. Birge, *J. Chem. Phys.* **73**, 5314 (1980).
- <sup>37</sup>N. Liver, A. Nitzan, A. Amirav, and J. Jortner, *J. Chem. Phys.* **88**, 3561 (1988).
- <sup>38</sup>R. A. L. Vallée, M. V. D. Auweraer, F. C. D. Schryver, D. Beljonne, and M. Orrit, *ChemPhysChem* **6**, 81 (2005).
- <sup>39</sup>G. McDermott, S. M. Prince, A. A. Freer, A. M. H. Lawless, M. Z. Papiz, R. J. Cogdell, and N. W. Isaacs, *Nature (London)* **374**, 517 (1995).
- <sup>40</sup>A. Freer, S. Prince, K. Sauer, M. Papiz, A. H. Lawless, G. McDermott, R. Cogdell, and N. W. Isaacs, *Structure (London)* **4**, 449 (1996).
- <sup>41</sup>T. Polívka, D. Niedzwiedzki, M. Fuciman, V. Sundström, and H. A. Frank, *J. Phys. Chem. B* **111**, 7422 (2007).