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Voigt Profile Analysis and Band-Shape Parameter Dependence on Temperature and Solvent Dynamics in Absorption Spectra of Beta-Carotene

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ABSTRACT. We investigated joint influence of lifetime and solvent broadening, represented by Voigt profile, for absorption spectra of beta-carotene in acetone, ethanol and isopentane over a wide temperature range. The temperature and solvent dependence of the Gaussian contribution to the total width suggest that homogeneous solute-solvent interactions dominate, but inhomogeneous broadening and solvent structural effects are also important. The analysis provides good broadening parameters and displacement for strong active mode Ω_1 , whereas Ω_2 and Ω_3 displacements are poorly determined. Further specification of dimensionless shifts requires involving experimental data on the resonance Raman and coherent anti-Stokes Raman excitation profiles. Such analyses are in progress. © 2016 Bull. Georg. Natl. Acad. Sci.

Key words: carotenoids, Voigt profile, band-shape analysis

Beta-carotene is one of the most widespread natural molecules exhibiting a manifold of biological functions in a variety of organisms from bacteria and plants to animals. It plays a decisive role in photosynthesis due to its capability to absorb light in the region around 500 nm and to quench chlorophyll triplet states in photosystems in order to prevent the formation of highly reactive singlet oxygen. To understand the mechanisms of these processes it is essential to have a profound knowledge of the electronic properties of beta-carotene, especially of the involved electronic states.

The $A_{1g} \rightarrow B_{1u}$ transition of β -carotene gives a broad vibrationally resolved strong absorption band centred at 475-480 nm, depending on the solvent. Resonance Raman spectral analysis provided nuclear displacement parameters for the three dominating modes [1, 2]. Reported values do not agree in detail, but concurring conclusions are that Raman spectral patterns are dominated by Franck-Condon terms and the Ω_1 mode ($C = C$ stretch) is always associated with larger displacements than the Ω_2 and Ω_3 modes ($C - C$ stretch and deformation, respectively). Raman excitation profiles and absorption spectra for β -carotene also exhibit significant and characteristic solvent broadening [3].

Several theoretical analyses rested on the assumption that the broadening features arise from Lorentzian lifetime and inhomogeneous Gaussian broadening [1–4]. These models can often reproduce the data, but rely on static rather than dynamic view of the solute-solvent interaction. Solvent dynamics in the form of additional low-frequency displaced harmonic oscillators were incorporated in several other reports [5]. Low-frequency harmonic modes can indeed be precisely related to the inertial polarization components [6]. Environmental effects cannot, however, be represented only by Franck-Condon overall factors, but must also appear in the energy denominators of the scattering probability.

In order to illuminate the broadening features, we analyze the recorded absorption spectra by Voigt equations [7,8]. This profile is at first a convenient formal approach to the broadening features without associating specific mechanisms with two components. Gaussian band-shapes emerge, for example, both for inhomogeneous and homogeneous broadening in the strong-coupling limit. However, conversion of homogeneous band-shapes to include a lifetime term turns this band-shape into the Voigt profile. In this way the Gaussian extracted by Voigt profile analysis can be associated with dynamic solvent properties.

We consider first a two-level molecular system represented by a pair of potential surfaces spanned solely by a set of displaced harmonic collective solvent modes (a “linear” solvent). The probability per unit time for optical single-photon absorption is [6]:

$$W_{eg}(\nu) = (\beta |M_{eg}|^2 / i\hbar) \int_{-i\infty}^{i\infty} d\alpha \exp[-\Phi(\alpha) - \beta\alpha(\Delta F_{eg} - h\nu)], \quad (1)$$

where M_{eg} is the transition dipole, \hbar Planck’s constant ($\hbar = h / 2\pi$), $\beta = (kT)^{-1}$, k the Boltzmann constant, T the temperature, ΔF_{eg} the free energy gap between the two states and ν the incoming light frequency. $\Phi(\alpha)$ contains all information about the solvent dielectric dispersion and electronic charge displacement. In the high-temperature and strong-coupling limit $\Phi(\alpha)$ takes simple form:

$$\Phi(\alpha) = \beta\alpha(1-\alpha) (8\pi)^{-1} (\varepsilon_0^{-1} - \varepsilon_s^{-1}) \int d\vec{r} [\vec{D}_e(\vec{r}) - \vec{D}_g(\vec{r})] = \beta\alpha(1-\alpha) E_s \quad (2)$$

where E_s is the solvent reorganization free energy with ε_0 and ε_s optical and static dielectric constants, and $\vec{D}_g(\vec{r})$ and $\vec{D}_e(\vec{r})$ the molecular electric inductions in the ground and excited state, at the point \vec{r} .

The integration contour in eq. (1) is the most convenient along $\alpha = i\eta$. Consequently, we obtain:

$$W_{eg}(\nu) = (2\beta |M_{eg}|^2 / \hbar) \text{Re} \int_0^{\infty} d\eta \exp[i\beta(h\nu - E_s - \Delta F_{eg})\eta - \beta E_s \eta^2 - \beta\gamma\eta] \quad (3)$$

This form coincides with the known atomic spectral band-shapes subjected to both Doppler and lifetime broadening. From this observation $W_{eg}(\nu)$ can then be given by different forms suitable for spectral band-shape analysis. In particular, $W_{eg}(\nu)$ can be recast as a Voigt profile [7,8]

$$W_{eg}(\nu) = \frac{[M_{eg}]^2}{\hbar} \frac{\xi}{(\pi k T E_s)^{1/2}} \int_{-\infty}^{\infty} \frac{\exp(-y^2) dy}{\xi^2 + [y - (h\nu - h\nu_m) / 2(\pi k T E_s)^{1/2}]^2} \quad (4)$$

Where $h\nu_m = E_s + \Delta F_{eg}$ and $\xi = \gamma / 2(k T E_s)^{1/2}$. In [7,8] we have shown that the Voigt profile can also be integrated to rapidly converging sum

Table 1. Spectral band-shape parameters of the three-mode Voigt profile. Acetone solution. Energy in units of 10^3 cm^{-1} and the pre-factor A in units of $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$

	T(K)			
	180	221	251	297
$Q_{o_1}^2 / 2$	0.85 + 0.02	0.87 + 0.05	0.89 + 0.02	0.93 + 0.02
$(Q_{o_2}^2 + Q_{o_3}^2) / 2$	0.5 + 0.2	---	---	---
10^3 A	1.74 + 0.02	1.40 + 0.02	1.23 + 0.02	1.06 + 0.02
$2(kTE_s)^{1/2}$	0.44 + 0.01	0.54 + 0.02	0.63 + 0.01	0.68 + 0.01
ν_m	2.021 + 0.002	2.035 + 0.001	2.046 + 0.001	2.065 + 0.002
ξ	0.162 + 0.004	0.154 + 0.003	0.150 + 0.002	0.19 + 0.01

$$W_{eg}(\nu; \xi) = \frac{[M_{eg}]^2}{\hbar} \left(\frac{\pi}{kTE_s} \right)^{1/2} \left\{ \exp \left[\frac{-(h\nu - h\nu_m)^2}{4kTE_s} \right] [1 - \text{cth}(2\pi\xi)] \exp(\xi^2) \cdot \cos \left[\xi(h\nu - h\nu_m) / (kTE_s)^{1/2} \right] + \frac{2\xi}{\pi} \sum_{n=-\infty}^{\infty} (n^2 + \xi^2)^{-1} \exp \left[-\frac{n}{2} + \frac{(h\nu - h\nu_m)^2}{2(kTE_s)^{1/2}} \right] \right\} \quad (5)$$

The molar absorption coefficient, $k_{eg}^{(0)}(\nu)$ is obtained from the relation [6]

$$k_{eg}^{(0)}(\nu; \xi) = (2\pi / 3c) h\nu W_{eg}(\nu; \xi) \quad (6)$$

where c is the velocity of light in the solvent and the superscript “(0)” refers to the absence of molecular nuclear modes. This equation must be modified to incorporate the local mode Franck-Condon overlap factors and vibrational energy. For three harmonic displaced modes, appropriate to the absorption and scattering properties of β -carotene the overall molar absorption coefficient is

$$k_{eg}(\nu) = \exp \left[\sum_{i=1}^3 (Q_{oi}^2 / 2) \text{cth}(\beta \hbar \Omega_i / 2) \right] \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \sum_{n_3=0}^{\infty} \prod_{i=1}^3 \left\{ \exp(\beta n_i \hbar \Omega_i / 2) \frac{1}{n_i!} \left[\frac{Q_{oi}^2}{4sh(\beta \hbar \Omega_i / 2)} \right]^{n_i} k_{eg}^0(\tilde{\nu}; \xi) \right\} \quad (7)$$

Where $k_{eg}^{(0)}(\tilde{\nu}; \xi)$ is given by eqs. (4)–(6) with $\tilde{\nu} = \nu - \nu_m - (2\pi)^{-1} \sum_{i=1}^3 n_i \Omega_i$, $\{\Omega_i\}$ ($i=1-3$) are the frequencies, $\{Q_{oi}\}$ the dimensionless coordinate displacements of the three β -carotene modes, and the Voigt parameter ξ has been assumed to be identical for all the local mode states.

We now apply eq. (7) to the absorption data. Minimization must be undertaken with care since, in line with previous observations, the fits only reproduce the data approximately. The seven parameters are: The three molecular displacements, the Gaussian bandwidth, $\sigma = 2(kTE_s)^{1/2}$, ξ , ν_m and the pre-factor. The frequencies were taken as 1525, 1155 and 1005 cm^{-1} for the Ω_1 , Ω_2 and Ω_3 mode, respectively [1–3]. The

Table 2. The same spectral band-shape parameters as Table 1. Ethanol solution

	T(K)			
	162	202	252	294
$Q_{o_1}^2 / 2$	0.91 + 0.007	0.93 + 0.04	0.96 + 0.03	1.02 + 0.08
$(Q_{o_2}^2 + Q_{o_3}^2) / 2$	+ 0.2	---	---	---
$10^3 A$	0.48 + 0.01	0.44 + 0.01	0.36 + 0.01	0.28 + 0.02
$2(kTE_s)^{1/2}$	0.39 + 0.01	0.44 + 0.01	0.54 + 0.02	0.66 + 0.04
ν_m	2.029 + 0.001	2.043 + 0.003	2.060 + 0.001	2.073 + 0.001
ξ	0.22 + 0.01	0.24 + 0.01	0.219 + 0.001	0.191 + 0.002

following procedure was used:

- A calibration constant was first added to obtain a fit in the low-energy range. This was followed by a global fit with seven free parameters.
- A fit to the first peak was then carried out with σ , ν_m and the pre-factor as free parameters, the other parameters remaining at the values obtained from (1). This gives the best possible σ and ν_m .
- σ and ν_m thus obtained were used in a following fit in the low-energy range to obtain ξ and the additive constant.
- σ , ν_m , ξ and the additive constant were finally used to obtain the molecular displacements and the prefactor.

The procedure is prompted by the fact that σ and ν_m are more accurately determined than the nuclear displacements, and ξ most accurately by the band wings. Q_{o_2} and Q_{o_3} cannot be determined individually with reasonable accuracy since their frequencies are very close. The accuracy of $\{Q_{o_2}^2 + Q_{o_3}^2\}$ is better and only this combination is shown in the tables.

The parameters extracted from 200 data points are summarized in Tables 1-3. The following conclusions emerge:

- The procedure is adequate, but the best possible fits only reproduce the data approximately. Previous numerical analyses based on different broadening representations have also given approximate fits only.
- The Q_1 mode displacement is the largest, and only this mode is determined with satisfactory accuracy. The low accuracy of the Q_2 and Q_3 displacements is due to the profile insensitivity to Q_{o_2} and Q_{o_3} when these are significantly smaller than Q_{o_1} (see Fig. 1). The value of Q_{o_1} is close to several previous estimates from the Raman excitation profiles [1-4]. Q_{o_1} (and $0.5\{Q_{o_2}^2 + Q_{o_3}^2\}$) is virtually the same for the aprotic solvents, but increases slightly with increasing temperature. Q_{o_1} is about 10% higher in ethanol. This could suggest that the molecular modes are coupled weakly to solvent specific environmental modes.
- The parameter ξ is small and the vibronic peaks dominated by the Gaussian. ξ exhibits some solvent specificity. The corresponding lifetime broadening, γ , is smallest for isopentane where it decreases from 80 to 60 cm^{-1} between 122 and 290 K. γ is larger and increases with increasing T for the polar solvents, namely from 70 to 130 cm^{-1} in acetone and from 85 to 125 cm^{-1} in ethanol. The values are larger than the value of

Table 3. The same spectral band-shape parameters as Table 1. Isopentane solution

	T(K)				
	122	150	202	254	290
$Q_{o_1}^2 / 2$	0.83 + 0.05	0.84 + 0.02	0.86 + 0.02	0.87 + 0.02	0.91 + 0.02
$(Q_{o_2}^2 + Q_{o_3}^2) / 2$	0.51 + 0.04	0.49 + 0.03	0.5 + 0.1	0.4 + 0.2	0.4 + 0.2
$10^3 A$	1.90 + 0.03	1.63 + 0.03	1.47 + 0.02	1.28 + 0.01	0.4 + 0.2
$2(kTE_s)^{1/2}$	0.35 + 0.01	0.413 + 0.001	0.474 + 0.002	0.565 + 0.007	0.62 + 0.03
ν_m	2.029 + 0.001	2.040 + 0.002	2.059 + 0.001	2.078 + 0.001	2.093 + 0.001
ξ	0.22 + 0.01	0.19 + 0.01	0.16 + 0.01	0.12 + 0.01	0.10 + 0.02

50 cm⁻¹ for isopentane estimated from Raman excitation profiles when low-frequency Franck-Condon effects are included [2], but still in line with dephasing or nonradiative decay processes in the pico- or subpicosecond range Table 1.

D. The Gaussian bandwidths σ range from several to 600 cm⁻¹; they rise with increasing temperature, but σ is only proportional to T^{1/2} in the range 150 – 250 K. At lower T, σ approaches a constant in line with inhomogeneous, nonequilibrium broadening close to the freezing point. Local structure and correlated solvent motion are reflected in lower E_s than for structureless liquid. As T rises, the local structure is eroded, giving a larger E_s . This is compatible with a stronger T dependence of E_s for the polar solvents than for isopentane.

E. The Gaussian bandwidth is larger for acetone and ethanol than for isopentane. The simplest view of the solvent as structureless dielectric would give a width proportional to $(\epsilon_0^{-1} - \epsilon_s^{-1})^{1/2}$. This quantity is H^{0.7} at room temperature for both acetone and ethanol but vanishes for isopentane. The polar solvent bandwidths do in fact coincide at high temperatures, but the deviations at low temperature and strong discrepancy from the $(\epsilon_0^{-1} - \epsilon_s^{-1})^{1/2}$ relation for isopentane indicate the importance of local structural effects.

F. The E_s variation is only partly reflected in corresponding peak maximum variations ($h\nu_m \approx E_s + \Delta F_{eg}$). This discrepancy must be inherent in formal entropy components of ΔF_{eg} . The peak maximum is thus blue-shifted with the increasing temperature. The shifts amount to 60 cm⁻¹ for isopentane and 40 cm⁻¹ for the polar solvents over the temperature range investigated, while E_s from the bandwidth increases by 120 cm⁻¹ for isopentane, but peak shifts are in all cases much smaller, than the width increases. The correspondence is thus best for isopentane, but peak shifts are in all cases much smaller, than the width increases. The qualitative correlation still suggest that homogeneous, strong solute-solvent coupling (the “phonon” mechanism) is important, at least at higher temperatures.

ფიზიკური ქიმია

ბეტა-კაროტინის შთანთქმის სპექტრის მანასიათებელთა ტემპერატურასა და გარემოს დინამიურ ზემოქმედებაზე დამოკიდებულების შესწავლა ფოიგტის მრუდის გამოყენებით

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*ი.ჯავახიშვილის სახ. თბილისის სახელმწიფო უნივერსიტეტის რაგლადის არაორგანული ქიმიისა და ელექტროქიმიის ინსტიტუტი, თბილისი

(წარმოდგენილია აკადემიის წევრის გ. ცინცაძის მიერ)

ფოტოსინთეზირებად სისტემებში მნიშვნელოვანი ფუნქციონალური დატვირთვის გარდა, კაროტინოიდები გამოირჩევიან აქტიური თავისუფლების ხარისხის მინიმალური რაოდენობით, რაც ოპტიკური მეთოდებით მათ შესწავლას აადვილებს. შთანთქმის სპექტრები წარმოადგენს ელექტრონულ-რხვეითი (VIBRONIC) კომპონენტების სუპერპოზიციას, რომელთა ინტენსივობას და განაწილებას აქტიური თავისუფლების ხარისხის წანაცვლებები და სინშირეები განსაზღვრას. რაც შეეხება ვიბრონული მდგენელების ფორმას, ის განპირობებულია როგორც მოლეკულის შიდა რელაქსაციური პროცესებით, ასევე გარემოს დინამიური ზემოქმედებით და არაერთგვაროვნებით. სხვა ავტორთა თეორიული შრომების უდიდესი ნაწილი ეფუძნება დაშვებას, რომ ვიბრონული კომპონენტების ფორმირებაში ერთ-ერთი მექანიზმი დომინირებს და ის გაუსის ან ლორენცის ფუნქციით აღიწერება. იმის გამო, რომ გაუსისა და ლორენცის წვლილი პრაქტიკულად ყველა რეალური შემთხვევისათვის თანაზომადია, ჩვენი თეორიული მიდგომა გამოირიცხავს ასეთ აპრიორულ დაშვებას და ვიბრონული მდგენელებისათვის ფოიგტის ფუნქციის გამოყენებას ეფუძნება. ფოიგტის მრუდისათვის ჩვენ მიერ აღრეზიდებული ანალიზური გამოსახულების გამოყენებამ საშუალება მოგვცა რაოდენობრივი დათვლა მოგვეზინა დამატებითი პარამეტრის ვარირებით, რომელიც გაუსისა და ლორენცის ნახევარსიგანების შეფარდებას წარმოადგენს. ექსპერიმენტული წერტილებიდან თეორიული მრუდის გადახრის მინიმირების სტანდარტულმა პროცედურებმა ბეტა-კაროტინისათვის (აცეტონში, ეთანოლსა და იზოპენტანში), ტემპერატურის ფართო დიაპაზონში (122 K-დან ოთახის ტემპერატურამდე) მოგვცა რეალისტური მნიშვნელობები როგორც რელაქსაციური კონსტანტებისათვის, ისე გარემოს რეორგანიზაციის ენერჯიებისათვის. აღნიშნული პარამეტრებისათვის მიღებული თანაზომადი მნიშვნელობანი ცხადყოფენ ფოიგტის მრუდის გამოყენების აუცილებლობასა და ეფექტურობასზე.

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