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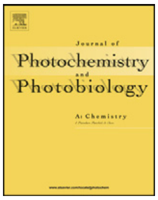

Absorption shifts in carotenoids—influence of index of refraction and submolecular electric fields

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ABSTRACT

Most biological functions of carotenoids relate to strong visible absorption. In a quest to protein matrix effects on spectra, the shifts produced by solvent refractive index (n) and static dielectric permittivity (ε) were quantified for visible absorption maxima of β-carotene and a model compound with sharper bands, tetra-*tert*-butylnonaene ttbP9. The dispersive red shift that depends on optical dielectric constant n^2 is insensitive to polarity, in disagreement with previous work (H. Nagae, et al., J. Chem. Phys. 101 (1994) 6750). Small residual red shift in polar liquids obtained after subtraction of the dispersive component, obeys a static susceptibility function $(\varepsilon - n^2)/(\varepsilon - n^2 + 4)$. Because polyenes show little inhomogeneous band broadening in polar solvents, the shift was assigned mainly to quadratic Stark effect, rather than to a reaction field of quadrupolar origin, proposed earlier (N. Ghoneim, P. Suppan, Spectrochim. Acta A, 51 (1995) 1043). It is highly plausible that the chromophore is polarized in short-range “edge fields”, according to molecular dynamics/semiempirical simulations (F. Cichos, et al., J. Chem. Phys. 114 (2001) 6824), not in a uniform cavity field, as usually presumed.

1. Introduction

Strong absorption of visible light by carotenoids is often associated with their biological functions, such as photosynthetic light harvesting in plants and bacteria, photoreception (phototaxis, vision), and protection from the light induced damage [1,2]. Coloration of bird feathers due to carotenes [3–5] is correlated with their internal, physiological functions [6–8]. Noninvasive spectroscopic methods constitute excellent means for precise characterization of color *in vivo*. However, the interpretation of data presupposes a fairly complete understanding of spectra *in vitro* model systems.

Spectroscopy of carotenes is already quite extensive [1,2,9]. Band shifts and broadening have been investigated in different liquids or polymers as a function of refractive index [10–15], static permittivity [11–15], temperature [13,16], pressure [17–20], and externally applied electric field [21–28]. Compounds with symmetrical end groups are formally devoid of dipole moment, and subject to universal dispersive interactions. The electrical moments induced in polar environment depend also on the polarizability of chromophore. In addition, it has been proposed that quadrupole moments of centrosymmetric molecules can produce local reaction fields by orienting solvent dipoles [29]. Spectral shifts occur, if electronic states connected with optical transition possess different stabilization energies (i.e. when polarizability or quadrupole moment changes after excitation). However, relative contributions of the above-mentioned solvent shift mechanisms (dispersion, polarization, interaction between charges) remain unknown.

Maxima of well-resolved absorption spectrum of 1,1,18,18-tetra-*tert*-butyl substituted nonaene (ttbP9) (Fig. 1) were reported recently for an extremely varied set of one hundred liquids [30]. These data proved very useful for quantitative analysis of solvent induced shifts, as well as for resolving several controversies existing in literature. First, band maxima were plotted as a function of solvent polarizability density, expressed as Lorenz–Lorentz function $\phi(n^2)$ of refractive index n. Small deviations in apolar solvents containing large amounts of F, S, and Cl were assigned to local polarizability variations [31,32]. The slope of the linear dependence of band maxima on $\phi(n^2)$ is not affected by static dielectric constant ε in highly polar liquids, in contrary to previous results [12,33]. Pure ε-dependent shift was separated, and found to be proportional to a “stretched” hyperbolic function of ε, rather than linear with ε, as predicted earlier for quadratic solvent Stark shifts by Nicol et al. [34]. Although the ε dependence can be approximated to a (quadrupolar) reaction field formula [29], the shift in polar media will be assigned to polarization in the cavity field, basing on little broadening in polar liquids. Nicol’s formula [34] is invalid, since the cavity field is not only fluctuating in time, but extremely nonuniform in submolecular dimensions [35].

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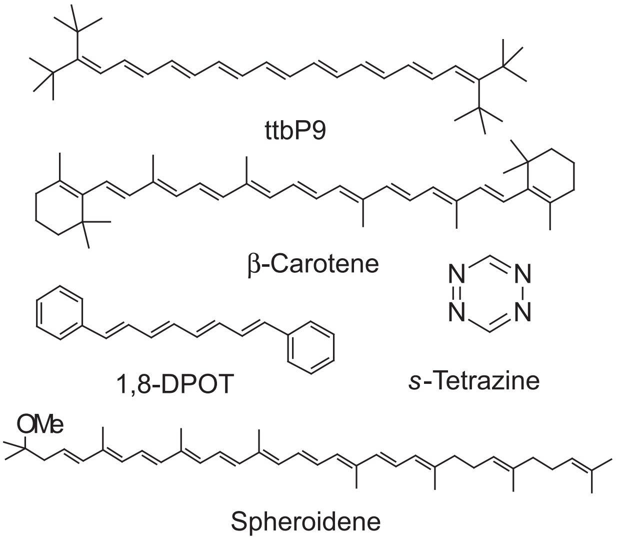

Fig. 1. Chemical structures of chromophores.

Functional pigments are always bound to proteins that can strongly affect spectral characteristics. A comparison to solutions could be invaluable for assessing the influence of more complex environments. A centrosymmetric marker dye, devoid of dipole moment, could probe fields as they exist *per se*, in contrast to dipolar molecules that are polarized preferentially in their own reaction fields. In this connection, we will address several controversies existing in the literature, concerning shifts caused by bulk refractive index and static permittivity [12,29,33,34].

2. Theoretical considerations

An expression for dispersive solvent shift has been derived by Bakhshiev from Lorenz–Lorentz and London equations [36,37]:

$$\Delta\nu_{\mathrm{disp}} = -\left(\frac{2}{3}\right) I_1 I_2 (I_1 + I_2)^{-1} \Delta\alpha r^{-3} \frac{(n^2-1)}{(n^2+2)} \tag{1}$$

where I_1 and I_2 are the ionization energies of the solute and solvent molecules, $\Delta\alpha$ is the difference between isotropic polarizabilities in the excited and the ground state, and r is the interaction radius. A calibration to experimentally measured $\Delta\alpha$ was necessary, in order to obtain a working formula from Eq. (1) [38]. It turned out that for chromophores of compact shape, such as aromatic hydrocarbons, r^3 (in Å^3) is numerically close to molecular weight M_{W}, leading to a correlation:

$$\Delta\nu_{\mathrm{disp}}\,(\mathrm{cm}^{-1}) = -5.5 \times 10^4\, \Delta\alpha M_{\mathrm{W}}^{-1} \frac{(n^2-1)}{(n^2+2)} \tag{2}$$

The studies in externally applied fields have revealed polarizability enhancement as large as 1000 Å^3 along the main axes of polyenes [21–28]. Accordingly, high sensitivity of the $1^1\mathrm{B_u}$ transition to refractive index of the solvent is expected, corresponding to large dispersive shifts of $\sim -10^4\,\mathrm{cm}^{-1}$ per unity Lorenz–Lorentz function $\phi(n^2)$ ($\phi(n^2) = (n^2-1)/(n^2+2)$) [10–15].

Polar solvents can be defined as those with static permittivity ε exceeding optical permittivity n^2 ($\varepsilon > n^2$), due to permanent molecular dipoles. Polarization of the guest molecule in the cavity field E_{c} would cause a red shift of absorption energy ($\Delta\nu_{\mathrm{pol}}$) (quadratic Stark effect):

$$\Delta\nu_{\mathrm{pol}} = \left(\frac{1}{2}\right) \Delta\alpha E_{\mathrm{c}}^2 \tag{3}$$

Previous researchers have assumed that the field influencing the chromophore is uniform, though with fluctuating magnitude and direction [34]. The homogeneous cavity field appears unlikely, particularly for a void accommodating long rod-shaped polyenic chromophores. Molecular dynamics/semiempirical simulation indeed reveal that electric field strength is high in the region of van der Waals contact between the solvent and solute molecules [35]. This "edge field" can act on difference polarizability density between two electronic states, producing a shift.

Another ε dependent shift is conceivable, if the quadrupole moment Q_{g} of a centrosymmetrical solute creates a reaction field, by means of preferential orientation of solvent molecules. According to Suppan's expression, a bathochromic shift would occur, if the quadrupole moment increases upon excitation [29]:

$$\Delta\nu_{\mathrm{q}}\,(\mathrm{cm}^{-1}) = -2(4\pi\varepsilon_0 hc)^{-1} \left[\frac{Q_{\mathrm{g}}(Q_{\mathrm{e}}-Q_{\mathrm{g}})}{r^5}\right] \times \left[\frac{\varepsilon-1}{\varepsilon+(1/2)} - \frac{n^2-1}{n^2+(1/2)}\right] \tag{4}$$

where ε_0 and h are electric and Planck constants, respectively, c is velocity of light, and Q_{e} is quadrupole moment in the excited state.

The interaction between the atomic charges of solute and solvent molecules has also been treated by a molecular dynamics/semiempirical calculation [35]. Shift components owing to polarization and the Suppan's mechanism were found to be of comparable magnitude for both the $\mathrm{S_1}$ and $\mathrm{S_2}$ transitions of naphthalene in acetonitrile. However, the results could not be properly tested, because the shift between apolar n-hexane and polar $\mathrm{CH_3CN}$ was difficult to extract from measured spectra, as a result of band broadening [35], and a comparison with the naphthalene vapour spectrum [39] was not attempted.

The separation of the quadratic Stark and the Suppan's effects is a challenging task, since the quadrupole moments of carotenoids seem to be unknown. Spectral shifts are accompanied by inhomogeneous broadening in disordered environments, such as glasses, liquids, and even proteins. Because of a vectorial dependence, the broadening is much stronger due to dipole–dipole, as well as multipolar interactions, as compared to polarization (and dispersion). Polyene bands broaden relatively little in polar liquids, so that the prevailing mechanism must be polarization by solvent dipoles.

3. Results and discussion

3.1. Refractive index dependent shift

Apolar solvents are defined as those with dielectric constant $\varepsilon \le 1.1n^2$. Absorption maxima ν display perfect linearity with regression coefficients $r > 0.997$ in homologous n-alkanes:

$$\nu = \nu_0 + p\phi(n^2) \tag{5}$$

The slope p, and intercept ν_0 that is close to transition energy of free chromophore in vacuum [31] are shown in Table 1 for ttbP9 [30], β-carotene [15], spheroidene [12], and 1,8-diphenyloctatetraene (DPOT). Branched (2-methylbutane, squalane), alicyclic (cyclohexane, decalin), and aromatic (benzene, tetralin, 1-methylnaphthalene, etc.) liquids fit very closely to the regression, drawn for normal alkanes (Fig. 2).

The deviating values for n-$\mathrm{C_6F_{14}}$ (no. 1), $\mathrm{CCl_4}$ (no. 71), and $\mathrm{CS_2}$ (no. 100) reflect different polarizability densities of heteroatoms, as compared to that of carbon, and other common atoms H, N, and O [31]. It is instructive to compare relative polarizability densities α/r_{w}^3, calculated from atomic refractivities R_{D} after Vogel ($R_{\mathrm{D}} = 4/3\pi N_{\mathrm{A}}\alpha$) [40,41], and van der Waals radii r_{w} for single-bonded forms of elements after Bondi [42] (Table 2). In perfluorinated solvents the shifts are less than expected from $\phi(n^2)$, because of small polarizability density of F atoms ($\alpha/r_{\mathrm{w}}^3 = 0.1$), with

Table 1
Refractive index dependence of absorption maxima[a].

Chromophore	ν_0 (cm^{-1})	$-p$ (cm^{-1})[b]	N	r	Solvents
ttbP9 S_2 (1^1B_u)[c]	23976 ± 24	9519 ± 98	12	0.99948	n-alkanes $C_{5\text{-}16}$
ttbP9 S_2 (1^1B_u)[c]	23820 ± 41	$\underline{8861}$ ± 155	27	0.9962	All apolar[d]
ttbP9 S_2 (1^1B_u)[c]	23631 ± 105	8928 ± 417	14	0.9872	Highly polar ($\varepsilon > 25$)
β-Carotene S_2 (1^1B_u)[e]	24555 ± 43	10134 ± 178	5	0.9995	n-alkanes $C_{5,6,9,12,16}$
β-Carotene S_2 (1^1B_u)[e]	24568 ± 137	$\underline{10155}$ ± 501	19	0.980	All apolar (– dioxane)
β-Carotene S_2 (1^1B_u)[e]	24133 ± 182	9577 ± 733	8	0.983	Highly polar ($\varepsilon > 25$)
Spheroidene S_2 (1^1B_u)[f]	22983 ± 60	10359 ± 241	12	0.9973	n-alkanes $C_{5\text{-}16}$
Spheroidene S_2 (1^1B_u)[f]	22455 ± 68	8974 ± 256	6	0.9984	Highly polar ($\varepsilon > 25$)
1,8-DPOT S_{20} (1^1B_u)[g]	27722 ± 61	$\underline{10056}$ ± 253	7	0.9984	n-alkanes $C_{5-9,11,16}$
1,8-DPOT S_{21} (1^1B_u)[g]	29158 ± 59	$\underline{9813}$ ± 244	7	0.9985	n-alkanes $C_{5-9,11,16}$
1,8-DPOT S_{22} (1^1B_u)[g]	30542 ± 76	$\underline{9738}$ ± 314	7	0.9974	n-alkanes $C_{5-9,11,16}$
s-Tetrazine S_1 (n–π^*)[g]	18162 ± 7	$\underline{1077}$ ± 28	7	0.9984	n-alkanes $C_{5-8,10,14,16}$

[a] Linear fitting parameters of Eq. (5): ν_0, intercept; p, slope of the solvatochromic plot; N, number of data points; r, correlation coefficient.
[b] Slope values used for dispersive shift correction (Eq. (6)) are underlined.
[c] Ref. [30].
[d] Omitting n-C_6F_{14}, dioxane, CCl_4, CS_2.
[e] Ref. [15].
[f] Ref. [12].
[g] This work.

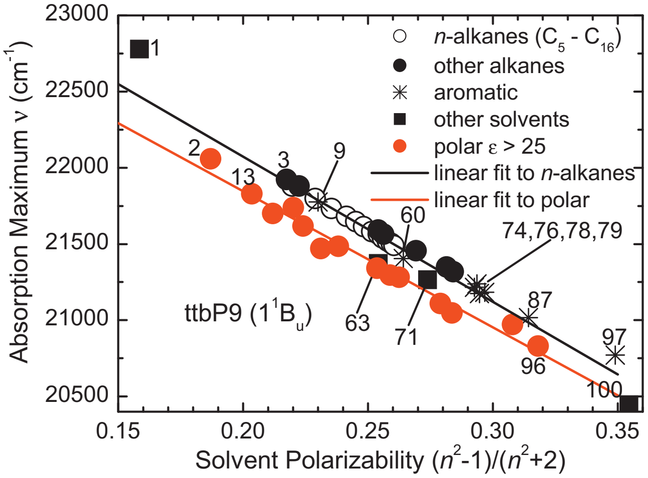

Fig. 2. Refractive index dependence of absorption maxima of tetra-*tert*-butylnonaene ttbP9 in apolar solvents ($\varepsilon \leq 1.15n^2$): open circles, n-alkanes form n-pentane to n-hexadecane; filled circles, other alkanes; asterisks, arenes (9: hexafluorobenzene; 60: 1,4-difluorobenzene; 79: benzene; 97: 1-methylnaphthalene); filled squares – other solvents (1: perfluorohexane, 63: dioxane, 71: CCl_4, 100: CS_2); and in highly polar aprotic solvents ($\varepsilon > 25$): filled red circles (2: trifluoroethanol; 13: acetonitrile; 96: nitrobenzene). Numbers correspond to Table 1 in Ref. [30].

respect to H, C, N, and O (0.20–0.29). By contrary, higher values of α/r_w^3 for Cl (0.43) and S (0.54) cause larger shifts in CCl_4 and CS_2. In these cases the bulk refractive index is not an adequate measure for local polarizability of atoms that are in van der Waals contact with the chromophore, and responsible for the major part of dispersive stabilization [31,32]. Fortunately, F and Cl are not found in proteins, and S is present in small quantities. Therefore, spectral shifts in protein environment should be well described by the Lorenz–Lorentz function [11,14], although pockets of less polarizable water and tight clusters of more polarizable aromatic residues may cause smaller anomalies.

Table 2
Atomic refractivities R_D, van der Waals radii r_w, and relative polarizability densities α/r_w^3 in aliphatic compounds[a].

Atom	R_D (cm^{-3})	α (Å^3)	r_w (Å)	α/r_w^3
H (in CH_2)	1.028	0.408	1.20	0.24
C (in CH_2)	2.591	1.028	1.70	0.21
N	2.744	1.088	1.55	0.29
O (in ethers)	1.764	0.70	1.52	0.20
F	0.81	0.32	1.47	0.10
S	7.921	3.14	1.80	0.54
Cl	5.844	2.32	1.75	0.43
Br	8.741	3.47	1.85	0.55

[a] R_D is from Ref. [40] ($R_D = 4/3\pi N_A\alpha$), r_w is the frequently used value for single bonded forms of elements from Table 1 in Ref. [42].

Spectra are shifted by ~300 cm^{-1} to lower frequencies in liquids with very high dielectric constants ($\varepsilon > 25$), from acetonitrile to nitrobenzene. The slope p of Eq. (5) is very slightly less than that in apolar solvents (by 6% for ttbP9 and 13% for spheroidene, Table 1). This small difference is explainable, since the guest–host interaction radius r in Eq. (1) is slightly compressed on going from hexane to hexadecane, as a result of increasing cohesion energy, or "internal pressure", that correlate with the size of solvent molecules, density, and boiling temperature.

A much larger difference in the slopes p has been reported between apolar and polar liquids for spheroidene (27%), so that the regression lines cross at $\phi(n^2) = 0.3$ (see Fig. 2 in Ref. [12]). It has been assumed that the polarizability difference $\Delta\alpha$ is suppressed in the cavity fields of polar media [12,33]. This seems unlikely, since, as a rule, nonlinear polarization leads to a weakening of the binding of electrons and nuclei, thus increasing polarizability in the high field. Apolar solvents used by these authors included CCl_4, CS_2, and several mixtures of n-hexane with CS_2. In addition to non-uniform polarizability density of these compounds, mixtures are subject to local enrichment in the vicinity of the chromophore by stronger solvating component (CS_2). Therefore, steeper slopes p constitute an artefact that should be corrected, thus rendering the following theoretical treatment [33] superfluous.

The electronic structure change of higher polyenes in polar environments is restricted to linear polarization. Otherwise, a change of $\Delta\alpha$ would cause a different slope p in apolar and polar sets (Eqs. (1) and (5)). Major rearrangements in the geometry and bond alternation can occur in this case [43]. Solvent driven modulation of $\Delta\alpha$ is possible for chromophores with large dipole moments, creating reaction fields that are by an order of magnitude stronger than the cavity fields. Nonlinear polarization accompanied by enhancement of dispersive shifts in polar solvents has recently been inferred for Reichardt's betaine [44].

By comparing the slopes of Eqs. (2) and (5), and using the relative molecular weight M_W of 537 for β-carotene, one obtains isotropic, or average $\Delta\alpha$ of about 100 Å^3. This value is by a factor of 2–3 less than expected for 1/3 of polarizability change that can be as large

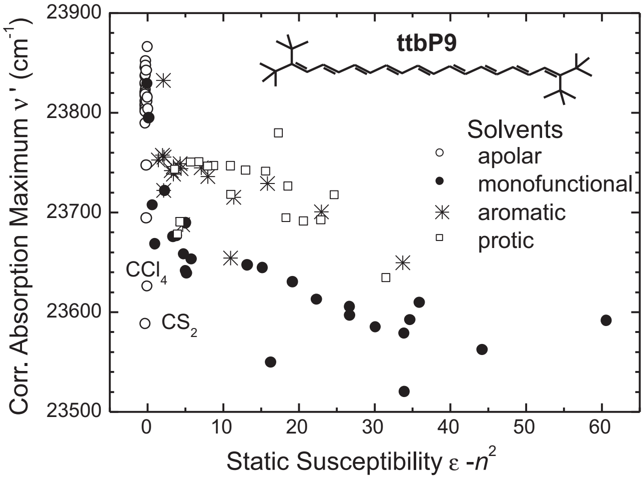

Fig. 3. Corrected (Eq. (6)) absorption maxima of tetra-*tert*-butylnonaene ttbP9 plotted versus the static susceptibility (open circles, apolar solvents; filled circles, aliphatic monofunctional solvents; asterisks, aromatic solvents; squares, protic solvents).

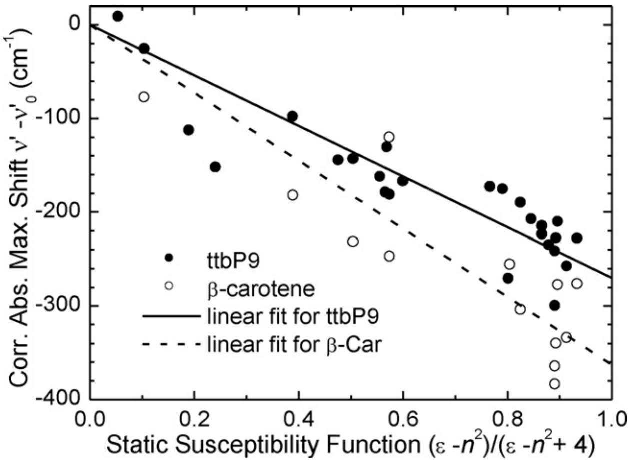

Fig. 4. Corrected (Eq. (6)) absorption maxima of tetra-*tert*-butylnonaene ttbP9 and β-carotene in monofunctional solvents plotted versus an empirical static susceptibility function (Eq. (9), $c = 4$).

as 1000 Å^3 along the transition dipole direction, or long axis of the molecule (the perpendicular polarizability components being negligible) [21–28]. The model of a polarizable sphere is obviously not applicable to strongly anisotropic chromophores where dispersion is better described as interaction between distributed polarizability densities.

Not less than 70% of dispersive solvent shift is generated in the closest layer of solvent molecules surrounding the chromophore, as evidenced by a line shift study in aggregates, formed in supersonic jets [45]. Consequently, the repulsive interactions must be taken into account, along with dispersive attraction. The problem was shortly discussed earlier [46,47], and will be treated in depth elsewhere. Concerning the present work, it is sufficient to accept that the shift components due to refractive index can be reliably separated from those depending on static dielectric constant ε.

3.2. *The (di)polarity dependent shift*

Solvent (di)polarity is characterized by the number of molecular dipoles per volume (concentration) and dipole moments that define dielectric constant ε [48,49]. Between apolar *n*-pentane and polar acetone, having the same refractive index, a considerable bathochromic shift occurs for ttbP9 [30], 1,8-DPOT, and spheroidene [12] ($-210 \pm 10\,\mathrm{cm}^{-1}$ for all), and β-carotene ($-285\,\mathrm{cm}^{-1}$) [15]. The dispersive effect that is solely a function of n can be separated by using the slope p, because of excellent fit to Eq. (5):

$$\nu' = \nu - p\phi(n^2) \qquad (6)$$

Corrected maximum positions ν' are plotted versus the difference between orientational and electronic susceptibilities $\varepsilon - n^2$ (that is close to ε, since $n^2 = 2 \pm 0.5$) in Fig. 3. Despite considerable scatter of data points, it can be seen that ν' obviously fails to show the linear dependence at larger ε, predicted earlier [34]. A theory by Nicol et al. for solvent Stark shift of spectra of nonpolar solutes in polar solvents leads to the following expression [34]:

$$\Delta\nu_{\mathrm{pol}} = 108\ln^2\left(\frac{R}{d}\right) R^{-3}\,\Delta\alpha k_{\mathrm{B}} T f_1(n^2, \varepsilon) \qquad (7)$$

where R is solvent shell radius, d is solute cavity radius, k_{B} is Boltzmann's constant, and T is temperature. It is easy to see that at high ε values the dielectric function $f_1(n^2,\varepsilon)$ becomes proportional to ε:

$$f_1(n^2, \varepsilon) = \frac{(\varepsilon - n^2)(2\varepsilon + n^2)}{\varepsilon(n^2 + 2)^2} \qquad (8)$$

Incidentally, the Onsager equation relates the concentration of dipoles and the dipole moment squared μ^2 to the same function $f_1(n^2,\varepsilon)$ (see Eq. (28) in Ref. [48] and Eq. (5.67) in Ref. [49]), but this expression is not applicable to liquids associated by means of hydrogen bonding. Accordingly, protic media (squares in Fig. 3) show smaller negative shifts than expected on the basis of ε. Satisfactory regression of S_1 (^1L_a) band maxima of anthracene and tetracene in Ref. [34] using Eq. (7) seems to be an artefact due to inclusion of alcohols and other protic solvents.

The range of liquids where solvation energies are well described in terms of Onsager's reaction field is obviously somewhat limited (for discussion see Section 24 in Ref. [49]), and should exclude, besides protic compounds, also strongly quadrupolar molecules, such as dioxane, aromatics, etc. [32]. A set of monofunctional solvents has been defined on the basis of aprotic and aliphatic compounds carrying a single prominent bond dipole, such as (mono)halogenides and nitriles, or several bond dipoles centered at a single atom (ethers, ketones, nitroalkanes, and DMSO), including esters and amides, but omitting oligohalogenides (e.g. $CHCl_3$), as C–H acidic and electron accepting [32,44]. The polarization shift in monofunctional solvents (filled circles in Fig. 3) can be approximated to a function:

$$\nu' = \nu'_0 + y'\left[\frac{\varepsilon - n^2}{\varepsilon - n^2 + c}\right] \qquad (9)$$

In most cases the best linearity is obtained with "stretching" factor c equal to 4 ± 1 (Fig. 4). Fitting parameters ν'_0 and y' are collected in Table 3, allowing one to compare the sensitivity of different transitions to ε.

Ghoneim and Suppan have found an approximate linearity with a similar function $(\varepsilon - 1)/(\varepsilon + 1/2)$, concluding that the solvent shift must originate from a reaction-field mediated solute quadrupole–solvent dipole interaction (Eq. (4)) [29]. Since the Nicols' formula (Eq. (7)) proved invalid, it was argued that cavity fields must play negligible role in solvatochromism [29]. However, alternative expressions exist for solute polarization by solvent dipoles that are close to "stretched" hyperbolic functions of ε, rather than linear with ε [50]. It is hardly possible to distinguish between the polarization and reaction field effects solely by means of fitting to different dielectric functions. To

Table 3
Solvent shift parameters as a function of static permittivity $(\varepsilon - n^2)/(\varepsilon - n^2 + 4)$[a].

Chromophore (transition)	ν'_0 (cm^{-1})	y' (cm^{-1})	N	r	Solvents[b]
ttbP9 S_2 (1^1B_u)[c]	23820 ± 5	−270 ± 28	50	0.964	apol(24 of 31) + mono(24)
ttbP9 S_2 (1^1B_u)[c]	23822 ± 8	−247 ± 16	72	0.883	apol(24) + polar aprotic(48)
β-Carotene S_2 (1^1B_u)[d]	24588 ± 11	−363 ± 21	28	0.961	apol(15 of 20) + mono(12)
β-Carotene S_2 (1^1B_u)[d]	24598 ± 15	−343 ± 27	46	0.884	apol(15) + polar aprotic(31)
1,8-DPOT S_{20} (1^1B_u)[e]	27701 ± 11	−241 ± 17	6	0.9905	C_5 + mono(5)
1,8-DPOT S_{21} (1^1B_u)[e]	29135 ± 14	−251 ± 20	6	0.988	C_5 + mono(5)
1,8-DPOT S_{22} (1^1B_u)[e]	30520 ± 66	−287 ± 24	6	0.986	C_5 + mono(5)
s-Tetrazine S_1 $(n–\pi^*)$[e]	18855 ± 40	379 ± 63	7	0.937	C_5 + polar aprotic(6)

[a] Linear fitting parameters of Eq. (9): ν'_0, intercept; y', slope of the solvatochromic plot; N, number of data points; r, correlation coefficient.
[b] apol, apolar; mono, monofunctional.
[c] Ref. [30].
[d] Ref. [15].
[e] This work.

aggravate the situation, data about quadrupole moments of polyenes in the ground and the excited states are not available.

The separation of these mechanisms may be possible by considering the ε-dependence of band broadening that is expected to be much larger in the case of multipolar interactions. For example, the blue shift of visible $n–\pi^*$ transition in *s*-tetrazine in polar solvents (see Fig. 4 in Ref. [51]) is perhaps an unambiguous case of Suppan's mechanism (Eq. (4)) [29]. The band has a relatively small negative shift of −209 cm^{-1} between the vapor phase and *n*-pentane. The slope p is equal to −1077 cm^{-1} (Table 1), in accordance with the dispersive shift formula (Eq. (2)) for $\Delta\alpha$ of 1.4 Å^3 in the gas phase [52] and size of molecule ($M_W = 82$). From these data, a small polarization induced red shift is expected. In reality, large hypsochromic effect of 360 cm^{-1} occurs between *n*-pentane and CH_3CN, corresponding to $y' = 379 \pm 63$ cm^{-1} in Eq. (9) (Table 3). In order to explain this up-shift of transition energy, a decrease of quadrupole moment in the excited state is required (Eq. (4)). Such diminishing is plausible, because the electron density is less extended in the π^* state.

Polarity causes dramatic spectral broadening in *s*-tetrazine, the double value of the half-width (2hwhm), measured on the low frequency side of the band increasing by ~500 cm^{-1}, from 210 cm^{-1} in C_5 to ~700 cm^{-1} in CH_3CN (data not shown). By contrast, the band width difference is only 110 cm^{-1} for ttbP9 between 2-methylpentane (2hwhm = 550 cm^{-1}) and dimethylsulfoxide (660 cm^{-1}) (see Fig. 1b in Ref. [30]). For 1,8-DPOT, the broadening of the first, 392 nm band is even less (50 cm^{-1}), from 740 cm^{-1} in C_5 to 790 cm^{-1} in CH_3CN.

Inhomogeneous broadening in disordered environments, such as liquids or glasses, arises as a result of a distribution of microscopic solvent shifts. Therefore, the solvent shifts of band maxima and band widths are correlated [53]. Dipole–dipole interaction can cause particularly strong broadening, because the sign of the shift is modulated by angular dependence. Polar chromophores embedded in polar matrix have the band width and the shift of comparable absolute magnitude [53]. In contrast, the polarization is insensitive with respect to vectorial characteristics of the field (Eq. (3)), and subject to less site-to-site fluctuations. Different broadening behaviour of *s*-tetrazine, and, on the other hand, that of $\pi–\pi^*$ chromophores, points to a change of solvatochromic mechanism. For polyenes, the shift in highly polar liquids, accompanied by small broadening must originate from polarization, rather than from multipolar interactions. However, the model of a uniform field (although fluctuating in time), filling a cavity of the size of a long polyenic chromophore appears unrealistic [35]. Instead, we should consider electric fields in subatomic dimensions, interacting with difference polarizability densities distributed over the solute.

4. Conclusions

We have traced and, in part, resolved several controversies in the liquid phase spectroscopy of polyenes that pertain also to proteins and other mesoscopic environments [12,29,33–35]. Dispersive shifts of spectra are almost perfectly correlated to Lorenz–Lorentz function $\phi(n^2)$, and independent on dielectric constant ε (polarity). Deviations occur in the media containing high proportion of F, Cl or S atoms, having very different polarizability densities, as compared to common H, C, N and O. The unfortunate use of hexane–CS_2 mixtures to tune refractive index has lead to excessively steep plots for spheroidene, neurosporene and β-carotene in apolar solvents, and to an erroneous conclusion that dispersive shift has been suppressed in polar liquids [12], followed by the *ad hoc* theory [33].

On the background of dispersive shift, a red shift caused by polarity is nearly by an order of magnitude smaller. Its dependence on dielectric constant obeys a function of static susceptibility $(\varepsilon - n^2)/(\varepsilon - n^2 + 4)$. The effect levels off fast with increasing ε that is in contradiction with Nicol's theory of quadratic Stark shift [34]. Alternatively, Suppan and Ghoneim have assumed that the shifts are exclusively due to quadrupolar reaction field (in polycyclic hydrocarbons) [29]. Distinguishing between the two mechanisms is possible by considering the polarity dependence of band widths. Little enhancement of inhomogeneous broadening indicates that the bathochromism of polyene absorption in polar environments must predominately be of polarization origin. However, the concept of quadratic Stark shift in a uniform cavity field [34] is invalid and should be replaced [35].

Refractive index is an adequate measure of polarizability of proteins and other biological environments, whereas static dielectric constant can hardly characterize internal fields under the circumstances when the mobility of polar groups is restricted. Local fields created by charged amino acids in proteins can be much higher than those existing in isotropic liquids. Carotene absorption will probe an effective field strength averaged over the size of the chromophore.

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