Gas-phase energy of the S2→S0 transition and electrostatic properties of the S2 state of carotenoid peridinin via solvatochromic shift and orientation broadening of absorption spectrum
Gas-phase energy of the $S_2 \rightarrow S_0$ transition and electrostatic properties of the $S_2$ state of carotenoid peridinin via solvatochromic shift and orientation broadening of absorption spectrum

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The solvent effect on the position and the shape of absorption spectrum of peridinin for 12 protic and aprotic solvents as well as the temperature effect for methanol were studied using a solvatochromic theory based on the Onsager sphere-cavity model. (Experimental data have been provided by T. Polivka and V. Sundström.) Solvatochromic calculations combined with estimations of orientation broadening of absorption spectrum by convolution allowed to conclude that the orientation (dipole-dipole), induction and dispersion solute-solvent interactions describe reasonably the position of the 0-0 frequency. The orientation interactions led to the blue solvatochromic shift, separating them from the induced and dispersion interactions, which produce red shift. The FWHM of Gaussian of inhomogeneous broadening originated from the fluctuations of orientation interactions is demonstrated to be high of 945 cm$^{-1}$ even for such nonpolar solvent as hexane. The value $|\Delta \mu|/\cos \varphi$ of -18.7 D has been found ($\Delta \mu = \mu_e - \mu_g$, $\varphi$ is the angle between $\Delta \mu$ and $\mu_g$). By assigning peridinin to the idealized $C_{2v}$ point group, the large change of dipole moment $|\Delta \mu|$ of 18.7 D under $S_2 \rightarrow S_0$ transition is obtained for peridinin in gas phase (for the solute free from environment). Moreover, the $S_2$ excited-state dipole moment $\mu_e$ has the opposite orientation relative to that at the ground $S_0$ state $\mu_g$. The determined gas-phase 0-0 energy of the $S_2 \rightarrow S_0$ transition of 22910 cm$^{-1}$ (2.84 eV) is employed to calculate the polarizability change between the $S_0$ and $S_2$ states of 376 Å$^3$. The finding for the effective Onsager radius is of 9.4 Å. Obtained results for electrostatic properties of $S_2$ state are compared with those known from Stark spectroscopy and quantum-mechanical calculations.

Introduction

Carotenoids serve a number of vitally important functions in various organisms. In photosynthesis, they act as light harvesters, as regulators of energy flows, as photoprotectors and antioxidants to prevent the generation of high-reactive singlet oxygen.$^{[1-7]}$ The protective effect is achieved not only through the rapid quenching of chlorophyll triplets, but also through direct deactivation of singlet oxygen. These unique functional abilities of carotenoids directly relate to their molecular structure resulting in atypical order of electronic levels. It is commonly assumed$^*$ that carotenoids, similar to polyenes, belong to the idealized $C_{2h}$ point group. The lowest excited state $2A_g^-$ is then forbidden for one-photon processes, because it carries gerade symmetry of the ground state $1A_g^-$. The strong absorption in the visible region
is due to allowed transition between the $1A_g^-$ state and the second excited state $1B_u^+$.\(^8,^9\) Existence of other optically forbidden states ($1B_u^-$ and/or $3A_g^-$) between the $2A_g^-$ and $1B_u^+$ states predicted theoretically for polyenes with six or more conjugated doubles bonds\(^10\), has been observed for some carotenoids in experiments.\(^11,^12\) Yet, for the carotenoid in this study, peridinin, both these states lies above the absorbing $1B_u^+$ state.\(^13\) Therefore, we will employ here the generally-used notation $S_0$, $S_1$, $S_2$ to denote the $1A_g^-$, $2A_g^-$, $1B_u^+$ states.

![Scheme 1. Molecular structure of peridinin.](image)

Peridinin (Scheme 1) is the principle carotenoid of the light harvesting complexes in dinoflagellates.\(^14,^15\) In the water-soluble peridinin-chlorophyll protein (PCP), peridinin even serves as a major light-harvesting pigment. It belongs to the family of carbonyl carotenoids whose conjugated carbonyl group alters significantly the excited-state properties by introducing an intramolecular charge transfer (ICT) state into the excited-state manifold.\(^16,^17\) The typical effect attributed to the presence of the ICT state is polarity-dependent lifetime of the lowest excited state. It has been shown that the lifetime of peridinin varies from 7 ps in highly polar solvents to 170 ps in the nonpolar solvents.\(^16-19\) The strong polarity dependence of lifetime peculiar also to uriolide acetate, fucoxanthin\(^17\) and especially to apocarotenals.\(^20-22\) Besides the polarity-dependent lifetime, energies and spectral profiles of the absorption and emission bands as well as the quantum yield of fluorescence are also highly affected by solvent environment.\(^16-23\)

In peridinin, the effects of the conjugated carbonyl group are among the strongest observed so far, which may be attributed to the location of the conjugated carbonyl group at a lactone ring and presence of the allene group in the $\pi$-electron conjugation. Molecular orbital calculations\(^13,^24\) suggested electron-charge density redistribution from the allene to the lactone upon the $S_2 \leftarrow S_0$ transition. Using the MNDO-PSDCI calculations Shima et al.\(^13\) concluded that the change of permanent dipole moment (DM) between $S_1$ and $S_0$ state comprises of 7.49 D. Their finding for DM at $S_1$ state by analysis of solvatochromic shift of absorption and fluorescence spectra was about 16 D in both polar and nonpolar environments with calculated DM at $S_0$ state of 5.97 D. In contrast to the MNDO-PSDCI calculation yielding change of DM for $S_2 \leftarrow S_0$ transition $\Delta\mu$ of 2.2 D\(^13\) significantly larger value of 22 and $\sim$27 D, at 77 K for peridinin in methyl tetrahydrofuran and ethylene glycol respectively, was found by Stark spectroscopy.\(^25\) Premvardhan et al.\(^25\) are noted that this results are supported by solvatochromic calculations when an ellipse-cavity model is employed. The large values of $\Delta\mu$ upon $S_2 \leftarrow S_0$ transition
were also obtained for another carbonyl carotenoid fucoxanthin.\textsuperscript{[26]} The negative $\Delta \mu$ of -6.18 D was recently obtained by Wagner et al.\textsuperscript{[27]} using the SAC-CI calculations for a peridinin model compound in methanol.

The change of DMs during absorption, radiative and nonradiative transitions between electronic states is closely allied to the ICT dynamics.\textsuperscript{[13,16-32]} However at the moment there is no clear consensus on both the CT nature of the excited states and on their DMs for peridinin. It should be also mentioned that there are a few reports\textsuperscript{[13,24,25]} dealing with calculations of peridinin intermolecular interactions in solutions. Onsager dipole-in-a-sphere model is used to estimate the dipole-dipole (orientation) solvation energy at the ground and excited states.\textsuperscript{[24]} Apart from analytical spectral-shift calculations for a number solvents\textsuperscript{[25]} the semiempirical calculations of level ordering were carried out for peridinin-water clusters\textsuperscript{[13]} as well as for six solvents\textsuperscript{[27]} in very simplified solvent-environment model. The large values of $\Delta \mu$ for the $S_2 \leftarrow S_0$ transition obtained by Stark spectroscopy, both for peridinin\textsuperscript{[25]} and related fucoxanthin,\textsuperscript{[26]} also added to a rebirth of interest in solvatochromic shift of peridinin absorption.

In this paper we show that the environment effect on the absorption spectrum can be adequately described by classical theory of intermolecular interactions through the application of the continuum Onsager model.\textsuperscript{[33]} The calculations provide the direct determination of DM and polarizability changes as well as the gas-phase 0-0 frequency for the $S_2 \leftarrow S_0$ transition. We argue that $\Delta \mu$ upon transition between $S_0$ and $S_2$ states of 18.7 D is negative, and that the DMs at the $S_0$ and $S_2$ states have opposite direction.

Theoretical backgrounds and results and discussion

1. Solvatochromic shift

Solvatochromic shift has its origin in the changes of both DM and polarizability of the solute upon absorption of light, provoking differential solvation energy of the ground and excited electronic states. We will ignore influence of repulsive interactions and H-bonding and write solvent dependent shift of the maximum position (or the 0-0 transition energy) of absorption spectrum as follows

$$
\Delta \nu = \Delta \nu_{or} + \Delta \nu_{ind} + \Delta \nu_{dis} =
$$

$$
= -\frac{2\mu_e (\mu_e - \mu_g)}{a_0^3} \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{(\mu_e - \mu_g)^2}{a_0^3} \frac{n^2 - 1}{2n^2 + 1} - \frac{3\Delta \alpha_{eg}}{a_0^3} \frac{E_{00}^2 I_s}{I_s - E_{00}^2} \frac{n^2 - 1}{n^2 + 2}.
$$

(1)

In eq. (1) the first two terms $\Delta \nu_{or}$ and $\Delta \nu_{ind}$ represent the solvatochromic shifts due to orientation and induction interactions adopted in accordance with Ooshika-Lippert-Mataga-McRae theory.\textsuperscript{[34-40]} The last term $\Delta \nu_{dis}$ represents a component of the shift due to dispersion interactions via formula derived in Ref [41]. The $\mu_e$, $\mu_g$, $\alpha_e$, $\alpha_g$ are the gas-phase DMs and polarizabilities of excited ($e$) and ground ($g$) states of
the solute molecule, respectively; \( \Delta \alpha_{eg} = \alpha_e - \alpha_g \); and \( E_{00} \) is the energy gap between \( e \) and \( g \) states for free (gas-phase) solute molecule; \( I_s \) is the ionization potential of solvent molecule; \( \varepsilon \) and \( n \) are dielectric constant and refractive index of the solvent. In the Onsager model\(^{[33]} \) a probe dipole is placed at the center of a spherical cavity. Therefore here the Onsager radius of the solute \( a_0 \) is an effective value, because for such linear molecule as peridinin the assumption of spherical shape of cavity is far apart from reality.

The following quantities will be used for convenience

\[
P_e = \frac{\varepsilon - 1}{2\varepsilon + 1}, \quad \Pi_n = \frac{n^2 - 1}{2n^2 + 1}, \quad P_n = \frac{n^2 - 1}{n^2 + 2},
\]

where \( P_e \) represents the bulk solvent polarity; \( \Pi_n \) and \( P_n \) represent two kinds of the bulk polarizability of solvent based on Onsager and Clausius-Mosotti treatment, respectively. There are three key unknowns in eq. (1):

\[
C_x = C_{or} = -\frac{2\mu_y(\mu_e - \mu_g)}{a_0^3},
\]

\[
C_y = C_{ind} = -\frac{(\mu_e - \mu_g)^2}{a_0^3},
\]

\[
C_z = C_{dis} = -\frac{3E_{00}^2 I_s^2 \Delta \alpha_{eg}}{I_s^2 - E_{00}^2 a_0^3} \Delta \alpha_{eg}.
\]

Using eqs. (1)-(4) the maximum (or 0-0 transition energy) of absorption spectrum may be given as

\[
\nu = \nu_0 + \Delta \nu = \nu_0 + C_x P_e + C_y \Pi_n + C_z P_n,
\]

where \( \nu_0 \) is a frequency absorption maximum (or 0-0 transition energy) in gas phase.

Dependence of absorption maximum on solvent polarizability \( P_n \) is plotted in fig. 1. As clear the good linear correlations of \( \nu_{max} \) versus \( P_n \) are obtained separately for polar and nonpolar solvents. By this is meant that \( P_n \) linearly depends on \( P_e \) and \( \Pi_n \) for these groups of solvents. Nevertheless, just here it should be noted that there is no escape from the conclusion that DM at the \( S_2 \) excited state of peridinin is distinct for nonpolar and polar media. Really, as is shown in fig. 1 (inset) the intersection point of regression line with ordinate \( \nu_{max} \) is 1350 cm\(^{-1} \) above for nonpolar solvents then that for polar ones. This difference of 1350 cm\(^{-1} \) is in complete agreement with the frequency of peridinin vibration being active in the optical transition.\(^{[18]} \) The reason is that for the high polar solvents, in contrast to nonpolar ones, the maximum of spectrum relates to the 0-0 transition. Consequently, in solvatochromic calculations it is necessary to employ the maxima of 0-0 bands \( \nu_{00} \) for all solvents which are presented as a function of \( P_n \) in fig. 2. Such plotting leads to minor intersection difference of 35 cm\(^{-1} \).

The absorption maximum \( \nu_{max} \) and position of 0-0 transition \( \nu_{00} \) of peridinin, along with the solvent parameters \( P_n, P_e, \Pi_n \), are listed in Table 1. After going from experimental \( \lambda \) to \( \nu \), when plotting, we have applied data \( \nu_{max} \) and \( \nu_{00} \) without rounding to preclude additional uncertainty under regression.
The standard deviation for $v_{\text{max}}$ and $v_{00}$ does not exceed 25 cm$^{-1}$. To estimate $P_n$, $P_\varepsilon$ and $\Pi_n$ the data for $\varepsilon$ and $n$ are were taken from handbooks\textsuperscript{[42-44]}. Next notations are used for solvents: $n$-hexane (Hex), $n$-heptane (Hept), benzene (Benz), carbon disulfide (CS2), diethylether (DEE), tetrahydrofuran (THF), 2-propanol (2Prop), methanol (MetOH), acetonitrile (ACN), ethylene glycol (EG), glycerol (Glyc), dimethyl sulfoxide (DMSO).

2. Orientation inhomogeneous broadening. Calculation of $C_x$, $C_y$, and $C_z$

To find the three unknowns $C_x$, $C_y$ and $C_z$ it is necessary to examine the broadening of absorption spectra resorting to convolution procedure. It is common knowledge\textsuperscript{[45,46]} that the fluctuations of orientation (dipole-dipole) solute-solvent interactions lead to inhomogeneous broadening of spectrum. Taking in attention eq. 3 the relation for the variance of maximum (or 0-0 transition energy) $D^2$ produced by orientation fluctuations can be expressed\textsuperscript{[46-49]} as

$$D^2 = \frac{2\Delta \mu^2}{a_0^2} - k_B T \frac{\varepsilon - 1}{2\varepsilon + 1} = -2C_y k_B T \varepsilon, \quad (6)$$

where $\Delta \mu = \mu_s - \mu_e$, $k_B$ is Boltzman constant, and $T$ is temperature. Notice, that the eq. (6) is in agreement with earlier general conclusion from Marcus\textsuperscript{[50]} that $D^2$ varies proportionally to $T$. Thus, the shape of observed spectrum $\kappa(\nu)$ is a convolution\textsuperscript{[46,51,52]}

$$\kappa(\nu) = \int_0^\infty d\omega \kappa_0(\nu, \omega) G(\omega - \omega_0) \quad (7)$$

between an individual absorber spectrum $\kappa_0(\nu, \omega)$ with maximum 0-0 band $\omega$ and the Gaussian inhomogeneous broadening

$$G(\omega - \omega_0) = \frac{1}{\sqrt{2\pi} D} \exp\left[ -\frac{(\omega - \omega_0)^2}{2D^2} \right]$$

with $D^2$ determined by eq. (6). The full width at half maximum (FWHM) of this Gaussian distribution is the inhomogeneous width of 0-0 band $\Gamma = 2\sqrt{2\ln 2} D$, and $\omega_0$ is a mean of $\omega$. It is noteworthy that $\kappa_0(\nu, \omega)$ is a function of both $\nu$ and $\omega$ simultaneously. To simplify calculations one considers a simplest case when the individual absorber has unchanged shape of spectrum for any one of $\omega$. The homogeneous broadening is always low and can be neglected. Since for the independent chance events the variances are summed additively\textsuperscript{[53]}, and having no any information about individual spectrum $\kappa_0(\nu, \omega)$, we employed spectrum for Hex (fig. 3, inset) in place of $\kappa_0(\nu, \omega)$ to find the relative variance $\Delta^2$ ($\Delta^2 = D^2_{\text{sol}} - D^2_{\text{Hex}}$) between Hex and any other solvent. To estimate $C_y$ and $D^2_{\text{Hex}}$ one write, on eq. (6), that

$$\Delta^2 = -2C_y k_B T \varepsilon - D^2_{\text{Hex}}.$$

\[\Delta^2 = -2C_y k_B T \varepsilon - D^2_{\text{Hex}}.\]
Following to convolution (7) the calculated spectra $\kappa(\nu)$ are fitted to those observed experimentally $\kappa_{\text{exp}}(\nu)$ for different solvents. The $\Delta^2$ have been determined when the spectra $\kappa(\nu)$ and $\kappa_{\text{exp}}(\nu)$ were equal in the total FWHM. The $\Delta^2$ obtained by such way depends on solvent polarity $P_e$ as shown in fig. 3. The numerical data for $\Delta^2$ are listed in Table 2 along with $D^2$ and $\Gamma$ at 293 K (as well for methanol at 190 K). Some examples of comparison of experimental and calculated spectra are shown in fig. 4.

One may see in fig. 3 that the relative variance $\Delta^2$ as a function of $P_e$ gives results conforming to linear dependence (8) for nonpolar solvents Hex, Hept, Benz and CS2 as well as for low polar solvents such as DEE and 2PrOH. The linear regression demonstrate the slope of 789110 cm$^{-2}$ with high correlation coefficient $r=0.9934$. Thus, we have concluded that for this group of solvents the relative broadening is mainly caused by the fluctuations of orientation interactions. Although the quite good liner correlation is observed, it does not include zero point, but this condition has to fulfill for the plot of $\Delta^2$ versus $P_e$ because $\Delta^2 = D^2 - D_{\text{hex}}^2$. On the other hand, the minor deviations between experimental $\kappa_{\text{exp}}(\nu)$ and calculated $\kappa(\nu)$ spectra are observed for CS2 (fig. 4). Consequently, the broadening of peridinin spectrum is described the best by eqs. (6) and (7) for CS2. On this basis we have employed the slope of 866160 cm$^{-2}$ for solid line connecting two points, Hex and CS2 (fig. 3) to found by eq. (8) $C_2=-866160/2k_B T_{\text{e}}=-2126$ cm$^{-1}$. Such way for handling data has outstripped all expectations. For Hex (Table 2), the variance $D^2$ of 161132 cm$^{-2}$ calculated by the second part of eq. (6) is in the excellent agreement with parameters of two-points line 866160$P_e$-161106 where the value of 161106 cm$^{-2}$ is $D_{\text{hex}}^2$.

Since $\Gamma_{\text{hex}} = 2\sqrt{2\ln 2} D_{\text{hex}}$ it immediately follows that the strong Gaussian inhomogeneous broadening with FWHM of 945 cm$^{-1}$ is generated by fluctuations of orientation interactions even for nonpolar Hex. Since for piridinin the $S_2$ lifetime remains a mystery one employs that of 50 fs known for the allied carotenoid fucoxanthin$^{[54]}$ to estimate the homogeneous width by the relation$^{[55]}$ $\Gamma_{\text{homo}} \approx (2\pi T_1)^{-1}$ ($T_1$ is the population decay time, the excited state lifetime). We obtain $\Gamma_{\text{homo}} \approx 100$ cm$^{-1}$ that is nearly one order of magnitude below then inhomogeneous broadening for Hex. Consequently, the homogeneous broadening can be ignored for all solvents under consideration. What’s more because the variance $\Delta^2$ was found as the relative value to Hex, our calculations assure a compensation of the component $\Gamma_{\text{homo}}$ despite the fact that the spectral line shape is Lorentzian.

The large deviations from eq. (6) in behavior of $\Delta^2$ are observed for highly polar solvents, MetOH, ACN, DMSO, EG, and for THF (fig. 3). The possible origins of deviations will be discussed below (section 8). Here one called also attention to other essential features. Whereas good fits of $\kappa(\nu)$ to $\kappa_{\text{exp}}(\nu)$ is realized for nonpolar solvents (Hex, Hept, CS2 and Benz), a characteristic feature of peridinin absorption spectrum in THF, 2Prop, MetOH, ACN, DMSO, EG and Glyc, is a superiority of the 0-0 transition intensity in the experimental spectrum $\kappa_{\text{exp}}(\nu)$ over that in spectrum $\kappa(\nu)$ calculated by
convolution (7) (fig. 4). This result suggests that individual absorber spectrum $\kappa(\nu,\omega)$ is still changed noticeably with variation of maximum 0-0 band $\omega$ (section 9).

To obtain the values $C_x$ one takes into account that two kinds of the bulk polarisabilities $P_n$ and $\Pi_n$ of Hex and 2Prop are practically equal, namely, 0.229 and 0.230 as well as 0.186 and 0.187 respectively. Inasmuch as dispersion and induced components of solvatochromic shift are equivalent for these two solvents, it is evident from eqs. (1) and (5) that $C_x=\frac{[\nu_{00}(2\text{Prop})^2\nu_{00}(\text{Hex})]}{[P_{\epsilon}(2\text{Prop})^2P_{\epsilon}(\text{Hex})]}=1358$ cm$^{-1}$. Under calculation the experimental $\nu_{00}(\text{Hex})$ of 20618.5 cm$^{-1}$ is used, while for 2Prop the $\nu_{00}(2\text{Prop})$ of 20990.5 cm$^{-1}$ have been estimated as 22864-8145.7$P_{\epsilon}(2\text{Prop})$ to achieve better accuracy (see captions to figs. 1, 2).

In the case of Hex, Hept and CS2 the good linear regression takes place with the slope of -9636 cm$^{-1}$ and very high $r$ of -0.9999 (fig. 2) for experimental data $\nu_{00}$ versus $P_n$. As is obvious from eq. (5), it is possible only when $P_\epsilon$ and $\Pi_n$ are linearly dependent on $P_n$. It should be particularly emphasized that there are two groups of points which include nonpolar solvents, Hex, Hept, Benz, CS2 (fig. 5), and polar ones, MetOH, ACN, 2Prop, EG, DMSO, Glyc. In either group, more or less, $P_\epsilon$ and $\Pi_n$ are linearly dependent on $P_n$, therewith for the latter group $P_\epsilon$ remains practically constant. DEE and THF take up intermediate position between these groups, and they are ignored under regression. We eliminated from consideration $\nu_{00}$ of Benz, which drops out from the first group unlike its position $\nu_{\max}$ in fig. 1. The minor cross-point difference of 35 cm$^{-1}$ for two groups of solvents (fig. 2) demonstrates the bright physical result, namely, when $P_n=0$ the peridinin molecules can be treated as though they are in gas phase, and $\nu_{00}$ must be alike. The linear plots $P_\epsilon$ versus $P_n$ as well as $\Pi_n$ versus $P_n$ with nearly equal slope of 0.595 ($r$ of 0.9991 and 0.9999 respectively) are exhibited in fig. 5 for Hex, Hept and CS2. Using these data the numerical estimation for the unknown $C_z$ of -9179 cm$^{-1}$ has been produced, on eq. (5), by the relation $C_z=-9636-0.595(C_x+C_y)$. Differently, we chose Hex, Hept and CS2 as a base for calculation of $C_z$ to use linear properties of eq. (5) under given $C_x$ and $C_y$. There is no need to discuss on what reason $P_\epsilon$ and $\Pi_n$ linearly depend on $P_n$ for these solvents because we solve pure mathematical task.

### 3. Gas-phase 0-0 electronic energy of the $S_2\leftrightarrow S_0$ transition

Full solvatochromic shift $\Delta \nu$ as well as its dispersion $\Delta \nu_{\text{disp}}$, orientation $\Delta \nu_{\text{or}}$ and induction $\Delta \nu_{\text{ind}}$ components are calculated according to eqs. (1), (5), when $C_x$, $C_y$, $C_z$ equal 1358, -2126, -9179 cm$^{-1}$ respectively. The findings are summarized in Table 1. It was desirable, where possible, to avoid errors, because of this the gas-phase 0-0 absorption maximum of 22910 (±40) cm$^{-1}$ was determined by plotting $\Delta \nu$ versus $\nu_{00}$ only for three base solvents, Hex, Hept and CS2. To account for such choosing, recall that peridinin spectrum for these solvents possesses well-resolved vibration structure (figs. 3, 4) that enables
to determine $v_{00}$ with acceptable accuracy and, thus, to preclude unnecessarily uncertainty for $v_{00}$ due to overlapping of 0-0 band with 0-1 one. Since the vibration bands in absorption spectrum of peridinin in solutions are separated by $\sim 1350 \text{ cm}^{-1}$, it is reasonable to assume that the 0-1 transition has the gas-phase energy about 24260 cm$^{-1}$. Fig. 6 provides the comparison of calculated 0-0 transitions $v_{\text{calc}}$ with experimental data $v_{00}$ and demonstrates the linear regression with slope of 1.0021 that, ideally, should be of 1.

5. Electric dipole moment at $S_2$ excited state. Effective Onsager radius

In view of lactone ring the polyene part of peridinin belongs to the $C_s$ point group, therefore the eqs. (2), (3) allow to determine only the value $|\Delta \mu|/\cos \varphi = 2\mu_y C_y/C_x$ ($|\Delta \mu| = |\mu_x - \mu_y|$), because we know nothing about $\varphi$, which may be an arbitrary value in the range from 0 to 180°. Nevertheless, the positive $C_x$ in eq. (2) is possible only when the angle $\varphi$ between $\mu_x$ and $\Delta \mu = \mu_x - \mu_y$ is greater then 90°. By using the ground-state DM of 5.97 D from Shima et al.$^{[13]}$, $C_x = 1358 \text{ cm}^{-1}$ and $C_y = -2126 \text{ cm}^{-1}$, one can obtain, that $|\Delta \mu|/\cos \varphi = 18.69 \text{ D}$.

As reported by Premvardhan et al.$^{[25]}$ the Stark spectroscopy measurements of peridinin in methyl THF yield, without the sign, the cosine of the angle between $\Delta \mu$ and the direction of the $S_2^{-} \rightarrow S_0$ transition dipole moment $m$ of 0.98. Consequently, to evaluate the DM in the $S_2$ state we can, at least for the $S_2^{-} \rightarrow S_0$ transition, relate the molecular structure of peridinin to the idealized $C_{2v}$ point group. The positive $C_x$ in this point group is possible only when $\varphi = 180°$. With this assumption one can find that the change of DM between $S_2$ and $S_0$ states, the component of $\Delta \mu$ in direction of $\mu_y$, is given as $\Delta \mu = 2\mu_y C_y/C_x$ to estimate $\Delta \mu$ of -18.7 D. Thus the gas-phase excited-state DM $\mu_2$ of 12.72 D is opposite to that of the ground state $\mu_g$. As indicated in fig. 6, there is no evidence that $\mu_2$ depends on solvent polarity because no essential deviations from the liner regression for all points (the slope is of 1.0708, $r=0.9862$). We have drawn the conclusion that $\mu_2$ is the same both in aprotic and protic solvents.

Our finding of 12.72 D for $\mu_2$ differs noticeably from that of 18 D from Premvardhan et al.$^{[25]}$ deduced from Stark spectroscopy result of 22 D by correction on a cavity field enhancement. The value $\Delta \mu$ of -18.7 D is far from that of -6.18 D presented by Wagner et al.$^{[27]}$ One further comment is in order that the SAC-CI calculations$^{[27]}$ predict only negative $\Delta \mu$ other then the opposite direction of $\mu_2$. (The remark in the Supporting material$^{[27]}$ “The dipole moments … in the case of the second and third excited singlet state are in roughly the opposite direction of the ground state dipole moment” is inconsistent with the numerical data, $\Delta \mu = -6.18 \text{ D}$ and $\mu_g = 8.67 \text{ D}$, presented in main part of paper in fig. 8, because $|\Delta \mu|$ is to be over $\mu_g$.

As follows from eq. (3)
that has enabled the effective Onsager radius \( a_0 \) of 9.4 Å to be determined. For comparison, one points out the long semi-axis of 13 Å employed in ellipsoid-cavity model.\(^{[25]}\) Very low value of 4.5-5 Å\(^{[29]}\) was based on the wrong assumption that the solvent effect is originated mainly from lactone ring and partially from polyene chain, while other parts of peridinin molecule are untapped.

6. Change of polarizability upon the \( S_2 \leftarrow S_0 \) transition

Since peridinin molecule is high anisotropic one, the polarizabilities \( \alpha_g \) and \( \alpha_e \) are the mean values determined as \( \alpha = \text{Tr} \alpha / 3 \), where \( \alpha \) is a polarizability tensor of the second order. We embarked on an effort to evaluate the \( \Delta\alpha_{eg} \) by eq. (4)\(^{[41]}\) employing relation

\[
\Delta\alpha_{eg} = -C_z \frac{I_s^2 - E_{00}^2}{3I_sE_{00}^2} a_0^3.
\]

The solvent ionization potential \( I_s \) is ranged from 9.25 (Benz) to 12.20 eV (ACN).\(^{[42]}\) When \( I_s \) of 10.4 eV taken as a mean for all solvents, \( \nu_{0,0} = 2.84 \text{ eV}, C_z = -9179 \text{ cm}^{-1} \) and \( a_0 = 9.4 \text{ Å}^3 \), one finds \( \Delta\alpha_{eg} \) of 376 Å\(^3\). With \( \alpha_g = 127 \text{ Å}^3 \) obtained for \( \pi \)- and \( \sigma \)-electrons\(^{13} \) the mean polarizability \( \alpha_e \) is of 503 Å\(^3\). Krawczyk and Olszowka\(^{[56]} \) have found by Stark spectroscopy measurements that \( \Delta\alpha \) ranged between 700-1600 Å\(^3\) for various carotenoids without lactone ring. Our value of 376 Å\(^3\) is lower due to the greater difference in molecular structure of compared carotenoids, since the high polar lactone ring causes a redistribution of the negative charge in polyene chain of peridinin. Such interpretation is supported by the Le Fevre rule\(^{[57]} \) that polarizability is markedly reduced whenever the \( \pi \)-electron conjugation system develops strong polarity. Thus, our result \( \Delta\alpha_{eg} = 376 \text{ Å}^3 \) is foolproof, though it is still larger than that of 179 Å\(^3\) calculated by the MNDO-PSDCI method.\(^{[13]} \)

7. Solvatochromism of peridinin

Solute-solvent coupling effects can be divided into non specific, or universal interactions and specific, or short-range interactions.\(^{[58]}\) The bulk influence of solvent as continuous media depends on dielectric constant \( \varepsilon \) and refractive index \( n \) of solvent, and thus manifests itself as universal interaction. Since the parameters \( C_y, C_z \) are negative, the induced and dispersion universal interactions give rises to the red (bathochromic) shift whereas the orientation interactions cause blue (hypsochromic) shift, because the \( C_z \) is positive. It is now possible to answer on the raised question whether the intermolecular repulsive interactions and H-bonding effect are negligibly small and can be ignored in solvatochromic shift for \( S_2 \leftarrow S_0 \) absorption. In all alcohols under consideration, regardless of their nature and structure, peridinin demonstrates solvatochromic shift for the most part from universal interactions because only minor
deviations are observed from the base line $\nu_{calc}$ versus $\nu_{00}$ plotted for Hex, Hept and CS$_2$ as well as from that for all solvents (fig. 6). This makes it possible to conclude that in protic media the specific interactions via H-bonding do not affect the position of the 0-0 transition.

Short-range repulsive interactions produce blue (hypsochromic) shift, but there is less information for organic compounds. The most extensively studies of repulsive solvent shift presented for $a'$I$_g \rightarrow X^3\Sigma^-$ phosphorescence of molecular oxygen.$^{[59,60]}$ As it was shown by Schmidt$^{[59]}$ the intermolecular repulsive interactions initiate blue shift of about 40 cm$^{-1}$, which more or less equal for different solvents. It is also known$^{[61]}$ that the $S_1$ excited-state changes of repulsion between oxygen of carbonyl group and environment for the derivative of 1,8-naphthalimide in diisopropyl ether breaks down the mirror symmetry between absorption and fluorescence spectra for active vibration of 630 cm$^{-1}$.

The results achieved in fig. 2 for peridinin show a little difference of 35 cm$^{-1}$ between linear regressions when $P_n=0$ for polar and nonpolar solvents. This minor cross-point difference lies in the limits of experimental error and should be not likely construed to distinction in repulsive effect. Contrary to the structure of molecular oxygen the conjugated system of peridinin is enough shielded from direct contact with solvent molecules and, as did, we can neglect repulsive solvatochromic shift at $S_2\leftarrow S_0$ transition.

As mentioned above, in Onsager reaction-field treatment$^{[33]}$ of solute-solvent interactions the solute dipole is placed at the center of a spherical cavity. We find that, despite a linear molecular structure of peridinin this simple model with effective cavity radius enables not only to separate out the dispersion, orientation and induced components of universal interactions, but also to find $\Delta\mu_{eg}$ and $\Delta\alpha_{eg}$. The assigning the molecular structure of peridinin to the idealized $C_{2v}$ point group has enabled to estimate the change of DM between $S_0$ and $S_2$ states $\Delta\mu$ of -18.7 D as well as the DM of the $S_2$ state $\mu_2$ of 12.72 D. Notably, our calculations show that the DM $\mu_2$ is opposite to that at the ground state $\mu_g$. It is needed to stress that the DM at the $S_2$ state $\mu_2$ does not depend from the nature of solvents at least for the Franck-Condon $S_2$ state. Some surprising data are presented in fig. 2, because they give an impression that peridinin exhibits two different forms in polar and nonpolar solvents. Therefore one have to keep in mind that, as already noted above, the $\nu_{00}$ depends not only on $P_n$, but on $\Pi_n$ and $P_c$ as good see from eqs. (1), (5). The minor intersection difference of 35 cm$^{-1}$ when the standard deviation is of 25 cm$^{-1}$ provides primary evidence that there is only one dominating form of peridinin in the ground state for all solvents or, again, the spectral difference between these forms dose not exceed 85-100 cm$^{-1}$. This is also to say that H-bonding in protic solvents leaves $\nu_{00}$ unaffected or exhibits a little spectral shift.

It is interesting to test if eq. (1) should be applicable for prediction of a thermochromic shift. The spectra of peridinin in MetOH measured at 293 and 190 K are shown in fig. 7. The value $\Delta n/\Delta T=4\cdot10^{-4}$ K$^{-1}$, $n_{293}=1.3270^{[42]}$ and one can find that $\varepsilon_{190}=66.24^{[43]}$. The eq. (5) predicts the red shift of 220 cm$^{-1}$
under cooling from 293 to 190 K when the evaluation of 170 cm\(^{-1}\) is a mean shift at half-width of spectra \((\delta_1 + \delta_2)/2\), in view of intensity redistribution between 0-0 and 0-1 bands. The orientation interactions provide blue shift under cooling while full red solvatochromic shift is accomplished together with induction and dispersion interactions. Despite the low precision of thermochromic shift observations, one can infer that eq. (1) predicts result with tolerable accuracy. Another important feature in the behavior of spectrum under cooling consists in the redistribution of intensity between 0-0 and 0-1 bands with a gain for the latter (fig. 7) that is discussed lower.

8. Anomalous spectral broadening

8.1. Fluctuations of microenvironment

For THF, MetOH, ACN, DMSO, EG and Glyc the relative variance \(\Delta^2\) is in strong disagreement with eq. (6), which carries out only for simple liquids, for nonpolar Hex, Hept, Benz, CS2 as well as for low polar DEE and 2PrOH. For Glyc the \(\Delta^2\) is so high, \(1.67 \cdot 10^6 \text{ cm}^{-2}\), that was not presented in fig. 3. This discrepancy indicates that in addition to the orientation broadening there are some other mechanisms of spectral broadening in called solvents. We emphasize that anomalous broadening occurs for self-associative solvents THF, ACN, MetOH, EG, Glyc as well as for DMSO. Owing to dielectric-loss microwave studies\(^{[62-64]}\) the OH---O self-association via H-bonding is the well-known phenomenon for alcohols. It may be safely suggested that in EG and Glyc contained two and three OH functional groups the anomalous broadening is caused by the variety of the branched OH---O-bonded networks which variously interact with peridinin, moreover via H-bonding with carbonyl group. That sets EG and Glyc apart from MetOH and especially from isomeric alcohol 2Prop, which possesses low affinity to H-bonding (fig. 3). High hygroscopic solvent DMSO demonstrates also the high relative variance, perhaps for a similar reason, because it offers ability in H-complexing with water, traces of which inevitably occurs in tested solution. In the theory of solvatochromism, Suppan\(^{[65]}\) has deduced that ACN belongs to self-associating liquids due to the forming non-dipolar dimers by pairing of dipoles. It is appropriate to add that such dipole-dipole interactions as the possible reason of cooperative reorientation of the ACN molecules have been considered\(^{[66]}\) to interpret the negative entropy of jump reorientation indicated at dielectric loss measurements. Neutron diffraction technique\(^{[67]}\) displays a preference for T-like configurations between the THF molecules at room temperature. Thus, we can conclude that the spectral broadening is more sensitive to the local structure of environment of peridinin molecule, whereas the peak position of spectrum is determined by bulk properties of solvent via \(\varepsilon\) and \(n\).

As early exhibited for retinyl compounds\(^{[68]}\), additional contribution to spectral broadening of carotenoids may be caused by the existence of conformers differing in their ring-side chain torsional angle. Such inhomogeneous broadening can not be ruled out because jet-cooled spectroscopy\(^{[69]}\) of
phenylbutadienyltrimethylcyclohexene gives an indication of conformers with torsional geometry. Nevertheless, one can assume that the effect of conformational disorder due to torsional motion, more or less, is the same for different solvents at the ground state, and there is compensation in variance $\Delta^2$ since it calculated by convolution (7) relative to Hex. Some others components of broadening, e.g. originated from the interaction with local phonons, are also nearly compensated in $\Delta^2$.

Brief mention should be made of red-shifted pump-probe transition spectrum observed in polar solvents by Zigmantas et al.\textsuperscript{19} for peridinin and Kosumi et al.\textsuperscript{54} for fucoxanthin under excitation in the red region. It was deduced\textsuperscript{16,54} that two spectroscopic forms, blue and red, exist in the polar environment. The H-bonding via carbonyl group is assumed\textsuperscript{19} to be the origin of the red form in protic solvents. We have used the theory of nonradiative transitions based on the bands-of-energy model of electronic levels\textsuperscript{46} to interpret the known data\textsuperscript{17,20,21} on the medium polarity effect on the $S_1(A_g^-)$ state lifetime of the apocarotenals\textsuperscript{70} and peridinin\textsuperscript{71}. We hold to the idea that the internal electric field from solvent environment heavily perturbs the molecules of pigments and changes their structure at $S_1(A_g^-)$ excited state after $S_2 \rightarrow S_1$ relaxation. In consequence of this the pigments possess the excited-state conformers. To take an example, the peridinin exists at $S_1(A_g^-)$ excited state as conformers I and II with very high DM of 40.7 and 42.8 D respectively.\textsuperscript{71} Nevertheless it is unjustified to link these conformers with steady-state absorption, because at the ground $S_0(A_g^-)$ state there is only one actual type of peridinin with strong orientation broadening due to the fluctuations of internal electric field in solution R. When pump-probe measurements are carried out the change of excitation energy selects the individual absorber under $S_2 \leftarrow S_0$ transition (well-known in the luminescence\textsuperscript{45,51,52} the red-edge effect) and thereby controls the internal electric field at $S_1(A_g^-)$ excited state (see also fig. 8). In the case of peridinin the internal electric field generates two types of excited-state conformers, I and II, but they are not generated for individual absorbers when $R$ is low or equals zero. For this reason either of the two conformers dominates in the solvents of different polarity and practically vanishes in nonpolar solvents. The nature of such conformers is discussed in Refs. [70, 71].

8.2. Shape variations of individual spectrum $\kappa_0(\nu,\omega_0)$

Under cooling a characteristic behavior of spectrum for MetOH consists in the strong transformation which involves the increase of intensity at 0-1 band and the decrease of that for 0-0 band (fig. 7). As indicated above, in polar solvents in contrast to nonpolar ones the maximum of absorption spectrum belongs to 0-0 transition. For polar solvents the convolution (7) shows also that the calculated spectrum has lower intensity of the 0-0 band than that from experiment (fig. 4). To understand these observations,
one considers more fully the behavior of spectrum \( \kappa_0(\nu,\omega_0) \) of individual peridinin molecule affected the internal electric field.

Shima et al.\textsuperscript{13} pointed out that all-trans conformer is preferentially populated in high-dielectric polar solvents such as CS\textsubscript{2} and MetOH. We support this evaluation, because the polar molecule of peridinin produces strong Onsager reaction field\textsuperscript{32,46}

\[
R_g = 2a_0^2 P \mu_g,
\]

of \( 8 \cdot 10^7 \) and \( 20.5 \cdot 10^7 \) V/m for nonpolar Hex and polar MetOH respectively \((a_0=9.4 \text{ Å}^3, \mu_g=5.97 \text{ D})\). We believe that all-trans conformer dominates in any solvents, because a reaction field stretches the solute molecule in line with its ground-state DM \( \mu_g \) nearly oriented along polyene chain \((\cos\theta=0.88)\). Hence it follows also that the shape of individual spectrum \( \kappa_0(\nu,\omega_0) \) depends on \( \omega_0 \) due to a different stretching of polyene chain at the ground \( S_0 \) state under the action of fluctuated internal electric field \( R \). Because the DM at \( S_2 \) state \( \mu_2 \) has the opposite direction to that at \( S_0 \) state \( \mu_g \), the stretching gives way to compressing at \( S_2 \) state under the \( S_2 \leftarrow S_0 \) transition. Some details of this interpretation are illustrated by the energy level diagrams in fig. 8. The changing from stretching to compressing (or vice versa) provokes the changes of Franck-Condon factor for the different individual absorbers (inset in fig. 8). The concrete numerical example of the change in the pigment length following excitation in \( S_1 \) state is described by Enriquez et al.\textsuperscript{72}, but the solvent can enhance or depress this effect versus the orientation of DM at the excited state.

According to the bands-of-energy model of electronic levels\textsuperscript{46} and as shown in fig. 8 the fluctuations of \( R \) provoke the variation of electronic energy and result in the continuum formation of orientation sublevels at the ground \( S_0 \) and excited \( S_2 \) states (sparse and equidistant horizontal thick lines). The \( R \) denoted the projections of chance internal electric field \( R \) on the DMs \( \mu_g \) and \( \mu_e \). The reaction field of medium \( R_g \) is mean determined by eq. (10). The orientation sublevels are placed lower or higher relative to the electronic level of pigment molecule unaffected by internal electric field, \( R_\mu=0 \). The equilibrium sublevel denoted as \( R_g \) is placed into the lower part of \( S_0 \) continuum. In this region \( R_g>0 \), and the internal electric field induces the stretching of solute molecule; and vise versa, the compressing is observed for the higher part of \( S_0 \) continuum. When the direction of peridinin DM is rotated to 180° under the \( S_2 \leftarrow S_0 \) transitions (vertical lines), the stretching of polyene chain at the \( S_0 \) state changes to its compressing at the \( S_2 \) state, because the projection of electric field \( R_\mu \) changes sing in strong accordance with Frank-Condon principle. The inset shows the parabolic potential energy diagrams and the changes of generalized coordinate \( \Delta q \) for 1350 cm\textsuperscript{-1} vibration mode via intrinsic repulsion. Thus, the internal electric field leads to a decrease of Huang-Rhys factor in going from blue to red absorbers. The relative intensities of 0-0, 0-1 and other vibration bands are shown by bold vertical lines. Under cooling as well as for more polar solvents the level \( R_g \) is lowering\textsuperscript{46} and the shape of
spectrum is changed towards the blue absorbers. Nevertheless, the full solvatochromic shift is red because of the induction and strong dispersion interactions (Table 1).

As may be inferred, eqs. (6) and (7), the redistribution of intensity between 0-0 and 0-1 in absorption spectrum depends from solvent polarity $P_ε$ and temperature $T$. Consequently, the 0-1 band dominates in spectrum for nonpolar solvents (fig. 4) and in cooled MeOH (inset in fig. 7).

Overall, we deduce that the anomalous spectral broadening in polar solvents has originates mainly in the fluctuations of microstructure and in the rearrangements into the solvation shell of peridinin due to specific interactions between solvent molecules. The fluctuations of the local structure in turn change the universal and short-range solute-solvent interactions. Anomaly is enhanced by the shape variation of individual spectrum $κ_{01}(ν,o_0)$ which is caused by fluctuation of internal electric field $R$.

**Conclusion**

There is good reason to think that the full solvatochromic calculations combined with convolution estimations of orientation broadening may be effective tool in study of electrostatic properties not only peridinin, but other carotenoids as well. The large change of DM $|Δμ|$ of 18.7 D under $S_2 ← S_0$ transition is corroborated by Stark spectroscopy research from Grondelle group.[25] The negative change of $Δμ$ relative to DM at the $S_0$ state have been demonstrated by the Birge group[27] via SAC-CI methods, however before our calculation the opposite orientation of $μ_2$ is conclusively not argued. We evaluated that the gas-phase 0-0 electronic energy of the $S_2 ← S_0$ transition $ν_{00}=22910 (±80) \text{ cm}^{-1} \ (2.84 \text{ eV})$. The error $±80 \text{ cm}^{-1}$ causes both the mistakes with regression and an uncertainty in repulsive and H-bonding effects. The obtained $ν_{00}$ provides the change of polarizability between $S_0$ and $S_2$ states $Δ\alpha_{eg}=376 \text{ Å}^3$ by eq. (9) in accordance with new formula for the dispersion solvatochromic shift[40]. In comparison with $ν_{00}$ of 2.84 eV the MNDO-PSDCI calculations[13] predict the energies of 1.96, 2.39 and 2.80 eV for the $A^-_g$, $B^+_u$ and $B^-_u$-like excited states respectively, in the case of all-trans conformer. It is worth noting that the resemblance with 2.80 eV for optically forbidden $B^-_u$-like state is accidental. It is likely that the EOM-CCSD methods are more accurate.[27] One would expect a further efforts will be required to perfect the quantum-mechanical calculations both transition energies and excited-state electrostatic properties. Of special interest are the angles between $μ_g$ and excited-state DMs. Based on the large change in DM we support opinion[25] that $S_2$ state ($B^+_u$-like) possesses CT character.

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**Key words:**

solvatochromic shift
excited-state dipole moment
excited-state polarizability
spectral broadening
peridinin
Figure 1. Experimental absorption maximum $\nu_{\text{max}}$ as a function of the solvent polarizability $P_n$. The linear regressions obtained for Hex, Hept, Benz, CS2 as well as for MetOH, ACN, 2Prop, EG, DMSO, Glyc are $\nu_{\text{max}} = 24213.6 - 9749.8 P_n$ and $\nu_{\exp} = 22863.9 - 8145.7 P_n$ respectively. The points for DEE and THF do not take in attention under regression (see details in text). The inset shows a cross-point difference of 1350 cm$^{-1}$ at $P_n=0$.

Figure 2. Plots of 0-0 band maximum $\nu_{00}$ versus $P_n$. The linear regression $\nu_{00} = 22828.8 - 9636.1 P_n$ is presented only for Hex, Hept, and CS2 (lower solid line). The points for DEE, THF (triangles) and Benz do not take in attention under fitting. Other linear regression, $\nu_{00} = 22863.9 - 8145.7 P_n$, for MetOH, ACN, 2Prop, EG, DMSO, Glyc coincides with that shown in fig. 1. Cross-point difference is of 35 cm$^{-1}$. 
Figure 3. Dependence of the relative variance $\Delta^2$ on the solvent polarity $P_e$, and solid line with slope of 866160 cm$^2$ connecting two points, namely Hex (zero) and CS2 (64962 cm$^2$). The dash line shows the linear regression for Hex, Hept, Benz, CS2, DEE and 2Prop with slope of 789110 cm$^2$. The inset displays the spectrum of peridinin in Hex, which was used as a reference spectrum $\kappa_0(\nu,\omega)$ in eq. (7) to evaluate $\Delta^2$.

Figure 4. Examples of comparison of the normalized experimental $\kappa_{\text{exp}}(\nu)$ and calculated $\kappa(\nu)$ spectra (solid and dots respectively) for peridinin in CS2, 2Prop, ACN, MetOH (left panel), Benz, DMSO, DEE, EG (right panel). In order to make the best use spectra are displaced in ordinates.
Figure 5. The linear plots $P_{\varepsilon}$ versus $P_n$ as well as $\Pi_n$ versus $P_n$ for nonpolar solvents, Hex, Hept, Benz, CS2.

Figure 6. Comparison of calculated 0-0 transitions with experimental maximum $\nu_{00}$, in accordance with eq. (5) $\nu_{\text{calc}}=22909+1358P_{\varepsilon}-2126\Pi_n-9179P_n$. The solid line with slope of 1.0021 shows the linear regression for base solvent Hex, Hept and CS2, $r=1$. The dash line with slope of 1.0708 displays the linear regression for all points, $r=0.9862$. 
Figure 7. Changes in absorption spectrum of peridinin in MeOH under cooling. Solid and dot lines show spectra measured at 293 and 190 K respectively. Inset illustrates the enlargement around the maximum.

Figure 8. Effect of internal electric field $R$ on the vibronic absorption spectrum for blue and red individual absorbers in light of bands-of-energy model of electronic levels$^{[46]}$ (see details in text).
References and notes


[60] V. S. Pavlovich, Solvatochromic shift of the 0-0 phosphorescence band and change of polarizability in the $a^1\Delta_g \rightarrow X^2\Sigma_g^-$ transition in the oxygen molecule, *J. Appl. Spectrosc.*, 2007, **74**, 501–507.


Table 1. Experimental absorption maximum \( \nu_{\text{max}} \) and peak position of 0-0 transition \( \nu_{00} \), peak position of 0-0 transition calculated by eq. (5) \( \nu_{\text{calc}} \), bulk solvent properties \( P_n \), \( P_\varepsilon \) and \( \Pi_n \), full calculated solvatochromic shift \( \Delta \nu_{\text{calc}} \) and its dispersion \( \Delta \nu_{\text{dis}} \), orientation \( \Delta \nu_{\text{or}} \) and induction \( \Delta \nu_{\text{ind}} \) components for peridinin in solutions at 293 K. All values \( \nu \) and \( \Delta \nu \) (cm\(^{-1}\)) are rounded to 1 cm\(^{-1}\).

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Table 2. Relative variance \( \Delta^2 \) obtained by eq. (7) at 293 K, the variance \( D_{\text{solv}}^2 = \Delta^2 + D_{\text{hex}}^2 \), the variance \( D^2 \) calculated by eq. (6), and FWHM \( \Gamma = 2 \sqrt{2 \ln 2 D} \) for peridinin in solvents of different polarity \( P_\varepsilon \).

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