[November, 1988] © *1988 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 61, 3797—3800 (1988)* 3797

Theoretical Treatment of Solvent Effects on the Frequency Shifts of Fluorescence Spectra

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(Received April 14, 1988)

A theoretical expression for the solvent fluorescence spectral shifts of a neutral solute molecule has been developed by following the same treatment as in Abe's expression for solvent absorption spectral shifts (*Bull. Chem. Soc. Jpn.*, **54**, 327 (1981); **58**, 3415 (1985)). Compared with all previous applicable expressions being applied to only polar solute molecules, the present expression has the advantage that it can be applied to not only the polar solute molecules but also nonpolar solute molecules. The polarizabilities of the ground and excited states concerning fluorescence are treated as being different from the corresponding values concerning absorption. Applications to nonpolar solute molecules are successfully presented.

Many theories have hitherto been proposed for solvent effects on the frequency shifts of fluorescence spectra.[1–10] All presented theoretical expressions are easily applicable except Liptay's.[4] Liptay's expression is so complicated that it is practically difficult to apply. Among the theoretical expressions, the first-appearing expression presented independently by Mataga et al.[1] and by Lippert[2] has been famous and frequently used. However, all these applicable expressions give no frequency shifts for nonpolar solute molecules having no dipole moments in both the ground and excited states, though some frequency shifts are, in fact, observed even for the nonpolar solute molecules in nonpolar solvents. In this case, the frequency shifts are obviously due to dispersion effects. Accordingly, the dispersion effects should be considered in the applicable theoretical expression for the solvent fluorescence frequency shift.

In this paper, therefore, an attempt has been made to present an expression for the solvent fluorescence spectral shift of a neutral solute molecule by explicitly considering the dispersion forces between the solute and solvent molecules on the basis of a previous theory[11] for the solvent absorption spectral frequency shift.

Theory

Fluorescence spectra of solutions are generally measured at very low concentrations of solutes. Let us, therefore, consider a system consisting of a spherical neutral solute molecule and N identical spherical neutral solvent molecules. The solvent molecules are assumed to form no hydrogen bonds or complexes with the solute and to have sufficiently small dipole moments so that they are not tightly oriented with respect to each other. In the fluorescence spectral measurements of solutes in solution, one usually chooses solvents that absorb light at much shorter wavelengths than the solutes do. One, therefore, assumes that the solvent molecules remain in their ground states when a transition from the ground state to the i-th excited state occurs in a solute molecule.

Then, one can write the ith electronic state of the system in the zeroth-order as

$$\Phi_i^\circ = \phi_i^{\mathrm{A}} \prod_{s=1}^{N} \phi_0^s. \tag{1}$$

Here, the zeroth-order wave functions of ϕ_i^{A} and ϕ_0^s denote the i-th state of the solute and the ground state of the s-th solvent molecule, respectively. In the present paper, the suffices and shoulders of A and s denote the solute and the s-th solvent molecule, respectively. The energy of the i-th state of the system in which all the molecules interact with one another can be written by the second-order perturbation theory as

$$E_i = E_i^\circ + (\Phi_i^\circ|\boldsymbol{H}'|\Phi_i^\circ) + \sum_{m\neq i} \frac{(\Phi_m^\circ|\boldsymbol{H}'|\Phi_i^\circ)(\Phi_i^\circ|\boldsymbol{H}'|\Phi_m^\circ)}{E_i^\circ - E_m^\circ}, \tag{2}$$

where E_i° and E_m° are the unperturbed energies corresponding to Φ_i° and the m-th excited state, respectively, of the system, and $\boldsymbol{H}'$ is the perturbation due to interactions among the molecules in the system. The wave function and energy of the ground state of the system are obtained by replacing i by 0 in Eqs. 1 and 2, respectively.

From Ref. 11, one can write $\boldsymbol{H}'$ as

$$\boldsymbol{H}' = \boldsymbol{H}'_{\mathrm{A}s} + \boldsymbol{H}'_{st}, \tag{3}$$

where

$$\boldsymbol{H}'_{\mathrm{A}s} = \frac{1}{4\pi\varepsilon_0} \sum_{s=1}^{N} \boldsymbol{p}_{\mathrm{A}} \cdot \boldsymbol{T}_{\mathrm{A}s} \cdot \boldsymbol{p}_s \tag{4}$$

and

$$\boldsymbol{H}'_{st} = \frac{1}{8\pi\varepsilon_0} \sum_{s=1}^{N} \sum_{t=1}^{N} \boldsymbol{p}_s \cdot \boldsymbol{T}_{st} \cdot \boldsymbol{p}_t. \tag{5}$$

Here, ε_0 is the permittivity of vacuum, $\boldsymbol{p}$ the operator of dipole moment, $\boldsymbol{T}_{\mathrm{A}s}$ the dipole–dipole interaction tensor of $R_{\mathrm{A}s}^{-3}(\boldsymbol{I}-3R_{\mathrm{A}s}^{-2}\boldsymbol{R}_{\mathrm{A}s}\boldsymbol{R}_{\mathrm{A}s})$, where $\boldsymbol{I}$ is a unit tensor, $\boldsymbol{R}_{\mathrm{A}s}$ the position vector from A to s, and t denotes the t-th solvent molecule.

When the wavenumbers of the fluorescence frequencies (cm^{-1}) of the solute molecule in vapor and in a solution are denoted by σ_{i0}° and σ_{i0}, respectively, one obtains the following expression for the solvent fluorescence spectral frequency shift:

$$\sigma_{i0} - \sigma^{\circ}_{i0} = \frac{1}{hc}\{<E_i - E^{\circ}_i>_{\mathrm{av}} - <E_0 - E^{\circ}_0>_{\mathrm{av}}\}, \quad (6)$$

where c is the speed of light in vacuum, h Plank's constant, and $< >_{\mathrm{av}}$ denotes the average over-all orientations of all the solvent molecules. In the calculation of $<E_i - E^{\circ}_i>_{\mathrm{av}}$, terms containing powers higher than the sixth power of $1/R$ may always be neglected. Moreover, for convenience, common terms appearing in both $<E_i - E^{\circ}_i>_{\mathrm{av}}$ and $<E_0 - E^{\circ}_0>_{\mathrm{av}}$ may be omitted in a calculation of $<E_i - E^{\circ}_i>_{\mathrm{av}}$.

Calculations of the terms of Eq. 6 will briefly be shown below. Using Eqs. 3—5, one can write:

$$(\boldsymbol{\Phi}^{\circ}_i | \boldsymbol{H}' | \boldsymbol{\Phi}^{\circ}_i) = \frac{1}{4\pi\varepsilon_0} \sum_{s=1}^{N} \boldsymbol{p}^{\mathrm{A}}_{ii} \cdot \boldsymbol{T}_{\mathrm{A}s} \cdot \boldsymbol{p}^{s}_{00} + \frac{1}{8\pi\varepsilon_0} \sum_{s=1}^{N} \sum_{t=1}^{N} \boldsymbol{p}^{s}_{00} \cdot \boldsymbol{T}_{st} \cdot \boldsymbol{p}^{t}_{00}, \quad (7)$$

where $\boldsymbol{p}_{00}$ and $\boldsymbol{p}_{ii}$ are the ground and ith-excited state dipole moments, respectively. Accordingly, considering the Franck–Condon principle, one obtains:

$$\begin{aligned}
&<(\boldsymbol{\Phi}^{\circ}_i | \boldsymbol{H}' | \boldsymbol{\Phi}^{\circ}_i)>_{\mathrm{av}} \\
&= <(\boldsymbol{\Phi}^{\circ}_i | \boldsymbol{H}'_{\mathrm{A}s} | \boldsymbol{\Phi}^{\circ}_i) \ \exp\{-(\boldsymbol{\Phi}^{\circ}_i | \boldsymbol{H}' | \boldsymbol{\Phi}^{\circ}_i)/kT\}>_{\mathrm{av}} \\
&+ <(\boldsymbol{\Phi}^{\circ}_i | \boldsymbol{H}'_{st} | \boldsymbol{\Phi}^{\circ}_i) \ \exp\{-(\boldsymbol{\Phi}^{\circ}_i | \boldsymbol{H}' | \boldsymbol{\Phi}^{\circ}_i)/kT\}>_{\mathrm{av}} \\
&\approx -\frac{1}{(4\pi\varepsilon_0)^2 kT} \sum_{s=1}^{N} <(\boldsymbol{p}^{\mathrm{A}}_{ii} \cdot \boldsymbol{T}_{\mathrm{A}s} \cdot \boldsymbol{p}^{s}_{00})(\boldsymbol{p}^{\mathrm{A}}_{ii} \cdot \boldsymbol{T}_{\mathrm{A}s} \cdot \boldsymbol{p}^{s}_{00})>_{\mathrm{av}} \\
&= -\frac{2(p^{s}_{00})^2 (p^{\mathrm{A}}_{ii})^2}{3(4\pi\varepsilon_0)^2 kT} \sum_{s=1}^{N} \frac{1}{R^6_{\mathrm{A}s}}, \qquad (8)
\end{aligned}$$

where k is Boltzmann's constant and T the thermodynamic temperature. In the same way, one obtains

$$\begin{aligned}
&<(\boldsymbol{\Phi}^{\circ}_0 | \boldsymbol{H}' | \boldsymbol{\Phi}^{\circ}_0)>_{\mathrm{av}} \\
&= <(\boldsymbol{\Phi}^{\circ}_0 | \boldsymbol{H}' | \boldsymbol{\Phi}^{\circ}_0) \ \exp\{-(\boldsymbol{\Phi}^{\circ}_i | \boldsymbol{H}' | \boldsymbol{\Phi}^{\circ}_i)/kT\}>_{\mathrm{av}} \\
&\approx -\frac{2(p^{s}_{00})^2 (\boldsymbol{p}^{\mathrm{A}}_{00} \cdot \boldsymbol{p}^{\mathrm{A}}_{ii})^2}{3(4\pi\varepsilon_0)^2 kT} \sum_{s=1}^{N} \frac{1}{R^6_{\mathrm{A}s}}. \qquad (9)
\end{aligned}$$

On the other hand, the calculation of the average value of the second term of Eq. 2 is quite the same as in the case of the absorption.[11] Thus, following the procedure given in Refs. 11 and 12, one finally obtains the following expression for the fluorescence frequency in solution:

$$\begin{aligned}
\sigma_{i0} = \sigma^{\circ}_{i0} &+ \frac{\pi}{hc}\left(\frac{4\pi L}{3}\right)^{2/3} \times \frac{(d^{\mathrm{s}}/M^{\mathrm{s}}_{\mathrm{r}})^{2/3}(p^{\mathrm{s}}_{00})^2}{(r_{\mathrm{A}} + r_{\mathrm{s}})^4} \\
&\times \left[\frac{2\{(\boldsymbol{p}^{\mathrm{A}}_{00} \cdot \boldsymbol{p}^{\mathrm{A}}_{ii}) - (p^{\mathrm{A}}_{ii})^2\}}{3(4\pi\varepsilon_0)^2 kT} + \frac{(\alpha^{\mathrm{A}}_{00,\mathrm{F}} - \alpha^{\mathrm{A}}_{ii,\mathrm{F}})}{4\pi\varepsilon_0} \right] \\
&+ \frac{\pi}{hc(4\pi\varepsilon_0)}\left(\frac{4\pi L}{3}\right)^{2/3} \times \frac{(d^{\mathrm{s}}/M^{\mathrm{s}}_{\mathrm{r}})^{2/3}\alpha^{\mathrm{s}}_{00}}{(r_{\mathrm{A}} + r_{\mathrm{s}})^4} \\
&\times [\{(p^{\mathrm{A}}_{00})^2 - (p^{\mathrm{A}}_{ii})^2\} + \frac{3}{2} \\
&\times \frac{I^{\mathrm{s}}_0 \cdot I^{\mathrm{A}}_0}{I^{\mathrm{s}}_0 + I^{\mathrm{A}}_0}(\alpha^{\mathrm{A}}_{00,\mathrm{F}} - \alpha^{\mathrm{A}}_{ii,\mathrm{F}})], \qquad (10)
\end{aligned}$$

where L is Avogadro's constant, M_{r} the relative molecular mass, d the density, α_{00} and α_{ii} are the electric isotropic polarizabilities of the ground and excited states, respectively, and r is the radius of a spherical molecule. The suffix F for $\alpha^{\mathrm{A}}_{00,\mathrm{F}}$ and $\alpha^{\mathrm{A}}_{ii,\mathrm{F}}$ means that these polarizabilities are not those concerning the absorption, but those concerning the fluorescence (for the reason mentioned below). In Eq. 10, the average transition energy for all transitions from the ground state or the i-th excited state to all other excited states is assumed to be equal to the ionization potential of the ground state (I_0), as shown in Ref. 12.

According to only Eq. 10, it is practically impossible to evaluate three values for p^{A}_{00}, p^{A}_{ii} and $(\alpha^{\mathrm{A}}_{00,\mathrm{F}} - \alpha^{\mathrm{A}}_{ii,\mathrm{F}})$ from data for the solvent fluorescence spectral shifts. In order to apply Eq. 10 for the fluorescence, therefore, the dipole moments of the ground and i-th excited states appearing in Eq. 10 must be assumed to be equal to the corresponding dipole moments concerning the absorption, as is usually assumed in all previous theories for fluorescence. This assumption will be approximately fulfilled, if the nuclear equilibrium configuration of the i-th excited state does not significantly differ from that of the ground state. Then, the dipole moments appearing in Eq. 10 must be estimated in advance from data for the solvent absorption spectral shifts according to an expression for the solvent absorption spectral shift. Of course, in the case of a nonpolar solute molecule, values for σ°_{i0} and $(\alpha^{\mathrm{A}}_{00,\mathrm{F}} - \alpha^{\mathrm{A}}_{ii,\mathrm{F}})$ can be estimated according to Eq. 10.

The isotropic polarizability of the i-th excited state of the solute molecule is written as $\alpha^{\mathrm{A}}_{ii} = \{2/3(4\pi\varepsilon_0)\} \times \sum_{j \neq i} |\boldsymbol{\mu}^{\mathrm{A}}_{ij}|^2/(E^{\mathrm{A}}_j - E^{\mathrm{A}}_i)$, where $\boldsymbol{\mu}^{\mathrm{A}}_{ij}$ is the transition dipole moment from the i-th state to the j-th excited state. Here, we will discuss whether or not the ground- and excited-state polarizabilities concerning the fluorescence are equal to the corresponding values concerning the absorption.

First, for the present purpose we consider the value of $\boldsymbol{\mu}^{\mathrm{A}}_{ij}$ according to the conventional treatment of Orlandi and Siebrand[13] for the Herzberg–Teller coupling mechanism as follows. Here, the vibronic state involved in the transition of the solute molecule is written as

$$\psi_{iv}(q,Q) = \phi_i(q,Q)\chi_v^{(i)}(Q), \qquad (11)$$

where q and Q denote the sets of electronic and nuclear coordinates, respectively, so that i is an electronic quantum number and v a vibrational one. Then, according to Orlandi and Siebrand,[13] the transition dipole moment from $\psi_{iv}(q,Q)$ to $\psi_{jw}(q,Q)$ (where j and w are the electronic and vibrational quantum numbers, respectively) is approximately given by

$$\begin{aligned}\boldsymbol{\mu}_{ij,vw} &= <\chi_v{}^{(i)}|\boldsymbol{P}_{ij}(\boldsymbol{Q})|\chi_w{}^{(j)}> \\ &\approx \boldsymbol{P}_{ij}(\boldsymbol{Q}_0)<\chi_v{}^{(i)}|\chi_w{}^{(j)}> \\ &+ \sum_k[\sum_l(<\phi_j|\boldsymbol{P}|\phi_l><\phi_l|\partial/\partial \boldsymbol{Q}_k|\phi_i>)_{\boldsymbol{Q}_0} \\ &\times(\hbar/2\mu_k\omega_k)^{1/2}]\times<\chi_{w'}{}^{(j)}|\chi_v{}^{(i)}>, \qquad (12)\end{aligned}$$

where

$$\boldsymbol{P}_{ij}(\boldsymbol{Q})=<\phi_i|\boldsymbol{P}|\phi_j>;\ \boldsymbol{P}=\sum_\mu e\boldsymbol{r}_\mu, \qquad (13)$$

$\boldsymbol{r}_\mu$ being the position vector of the μ-th electron in the solute molecule, μ_k and ω_k denoting the reduced mass and angular frequency of induced mode k, respectively, and w' denoting the ω value in which mode k is excluded. Moreover, $\boldsymbol{Q}_0$ is a nuclear equilibrium configuration, about which $\boldsymbol{P}_{ij}(\boldsymbol{Q})$ is expanded. In the case of the absorption, $\boldsymbol{Q}_0$ should be a nuclear equilibrium configuration of the ground state and in the case of fluorescence, $\boldsymbol{Q}_0$ should be an equilibrium configuration of the i-th excited state.

Equation 12 shows that the value of $\boldsymbol{\mu}_{ij}$ varies with both the nuclear equilibrium configuration and the vibrational quantum number v in the i-th state, even if $\boldsymbol{P}_{ij}(\boldsymbol{Q}_0)=0$ for forbidden electronic transitions. Accordingly, the value of $|\boldsymbol{\mu}^A_{ij}|^2$ involved in the expression for the polarizability will vary with the equilibrium configuration and the vibrational quantum number v. Moreover, the polarizability of the i-th state will vary with the vibrational quantum number v through the change of the value of $1/(E^A_j-E^A_i)$ with v, because the E^A_i value varies with v. After all, the polarizability of the i-th state will vary with its equilibrium configuration and vibrational quantum number. In the same i-th electronic state, both the vibrational quantum number and equilibrium configuration of the vibronic state concerning the fluorescence may differ from the corresponding values of the vibronic state concerning absorption. These differences between the two vibronic states will cause differences between the polarizabilities of the vibronic states. Thus, the polarizabilities of the ground and i-th excited states concerning fluorescence will differ from the corresponding values concerning absorption. For this reason, the polarizabilities concerning fluorescence are clearly denoted by the subscript F in Eq. 10.

The transition energies (in cm^{-1}) of the solute molecule from the ground state to the i-th excited state in vapor and in a solution are denoted by σ°_{0i} and σ_{0i}, respectively. The polarizabilities of the ground and i-th excited states concerning absorption are denoted by $\alpha^A_{00,A}$ and $\alpha^A_{ii,A}$, respectively. For a nonpolar solute molecule having no dipole moments in both the ground and excited states, values for σ°_{0i} and $\alpha^A_{ii,A}$ can be obtained from data for the solvent absorption spectral shifts according to Ref. 12. By applying Eq. 10 to data for the solvent fluorescence spectral shifts of a nonpolar molecule, values for σ°_{i0} and $(\alpha^A_{00,F}-\alpha^A_{ii,F})$ can be obtained by the least-squares method. On the other hand, for a polar solute molecule, values for p^A_{ii} and $\alpha^A_{ii,A}$ ought to be obtained in advance (according to Ref. 12) on the condition that the σ°_{0i} value is known. Then, by using the p^A_{ii} value, values for σ°_{i0} and $(\alpha^A_{00,F}-\alpha^A_{ii,F})$ can be obtained by means of a least-squares analysis of data for the solvent fluorescence spectral shifts, according to Eq. 10.

Applications

Equation 10 improves on a weak point of all the previous expressions which can not be applied to nonpolar solute molecules. In this paper, therefore, examples of the applications of Eq. 10 to only nonpolar solute molecules of anthracene, *all-trans*-1,3,5,7-octatetraene and pyrazine will been shown below, although Eq. 10 was also successfully applied to some polar solute molecules.

In applying Eq. 10, as well as the expression for the absorption in Ref. 12, to nonpolar solute molecules, the temperature was always assumed to be 20 °C. All values used for $\alpha^A_{00,A}$ and α^S_{00} were calculated from values for molar refraction, which were obtained by summing up bond refractions. The calculations of r_A and r_s were made in the same way as in Ref. 12. The gas-phase dipole moments of solvent molecules and the ionization potentials of all the solute and solvent molecules, except octatetraene, were taken from the usual chemical handbooks. Only the ionization potential of the ground state of an octatetraene molecule having four conjugated double bonds was estimated to be 8.22 eV ($1\ eV=1.602\times10^{-19}\ J$) in the same way as in the case of a lycopene molecule,[12] since no observed ionization potential value for the molecule was found. The author excluded data for solvents lacking information regarding their ground-state dipole moments and ionization potentials and for solvents which are capable of forming hydrogen bonds and complexes with solutes.

According to the procedure described above, the expression for the absorption in Ref. 12 and Eq. 10 were applied to data for the solvent absorption- and fluorescence-spectral shifts, respectively, of anthracene,[14] *all-trans*-1,3,5,7-octatetraene[15] and pyrazine.[6] Values estimated for σ°_{0i}, σ°_{i0}, $(\alpha^A_{ii,A}-\alpha^A_{00,A})$ and $(\alpha^A_{ii,F}-\alpha^A_{00,F})$ are listed in Table 1. By using these values, values for σ_{0i} and σ_{i0} were calculated and compared with the corresponding observed values, as shown in Fig. 1. This figure shows that the correlation between the observed and calculated values of σ_{0i} and σ_{i0} is good.

Table 1 shows that the present values for σ°_{0i} and σ°_{i0} roughly approach the corresponding observed values. As shown in Table 1, the estimated value of $(\alpha^A_{ii,A}-\alpha^A_{00,A})$ for anthracene agrees well with the observed values measured by electric field tech-

Table 1. Differences in Polarizabilities between the Ground- and Excited-States of Nonpolar Molecules

	Anthracene	*trans*-1,3,5,7-Octatetraene	Pyrazine
$\sigma^{\circ}_{0i}/\mathrm{cm}^{-1}$	27470	34785	31460
(Obsd)	(27560)[a]	(35523)[b]	(30870)[c]
$(\alpha^{\mathrm{A}}_{ii,\mathrm{A}}-\alpha^{\mathrm{A}}_{00,\mathrm{A}})/10^{-24}\,\mathrm{cm}^3$	18.5	36.71	−2.35
(Obsd)	(16.7±2.3)[d]		
$\sigma^{\circ}_{i0}/\mathrm{cm}^{-1}$	27580	25666	29280
(Obsd)	(27380)[a]		
$(\alpha^{\mathrm{A}}_{ii,\mathrm{F}}-\alpha^{\mathrm{A}}_{00,\mathrm{F}})/10^{-24}\,\mathrm{cm}^3$	25.1	6.90	2.76

a) Ref. 14. b) Ref. 15. c) Ref. 16. d) Refs. 17 and 18.

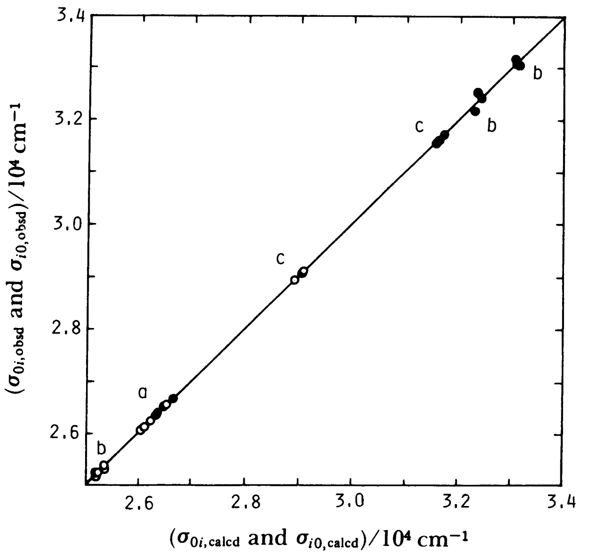

Fig. 1. Correlation between the observed and calculated values of σ_{0i} (●) and σ_{i0} (○), for anthracene (a), *all-trans*-1,3,5,7-octatetraene (b) and pyrazine (c).

niques.[17,18] The present result of $\alpha^{\mathrm{A}}_{00,\mathrm{A}}>\alpha^{\mathrm{A}}_{ii,\mathrm{A}}$ for pyrazine is probably due to the great contribution of the $|\mu_{i0}|^2/(E^{\mathrm{A}}_0-E^{\mathrm{A}}_i)$ term to the $\alpha^{\mathrm{A}}_{ii,\mathrm{A}}$ value, since $(E^{\mathrm{A}}_0-E^{\mathrm{A}}_i)<0$ in this case. Table 1 shows that the values for $(\alpha^{\mathrm{A}}_{ii,\mathrm{F}}-\alpha^{\mathrm{A}}_{00,\mathrm{F}})$ are considerably different from the corresponding values for $(\alpha^{\mathrm{A}}_{ii,\mathrm{A}}-\alpha^{\mathrm{A}}_{00,\mathrm{A}})$. This means that the ground- and excited-state polarizabilities concerning fluorescence are considerably different from the corresponding values concerning absorption. In the case of octatetraene, the absorption band is the 0–0 band. Therefore, the estimated value (51.51×10^{-24} cm^3) for $\alpha^{\mathrm{A}}_{ii,\mathrm{A}}$ is equal to $\alpha^{\mathrm{A}}_{ii,\mathrm{F}}$. In this case, therefore, the value for $\alpha^{\mathrm{A}}_{00,\mathrm{F}}$ can be estimated to be 44.61×10^{-24} cm^3, which is much greater than the $\alpha^{\mathrm{A}}_{00,\mathrm{A}}$ value (14.80×10^{-24} cm^3).

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