

A Statistical Model of Steady-State Solvatochromism

Olaf Roliński¹ and Aleksander Balter¹

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This work provides a description of the solvatochromic effect in terms of a hard-sphere model taking into account the microscopic parameters of the solution. The average energies of the solute-solvent system were calculated for Franck-Condon and relaxed states assuming pairwise electrostatic interactions between polarizable, dipolar molecules contained in clusters made of 1-solute and 10-solvent molecules. This in turn allowed us to estimate the values of the solvatochromic shifts. The dependence of these shifts on temperature and electronic properties of molecules expressed in terms of their polarity and polarizability was investigated.

KEY WORDS: Solute-solvent interactions; solvatochromic shift; thermochromic shift; coumarin 153.

INTRODUCTION

The solvatochromic effect is due to solute-solvent interactions and is particularly well manifested for polar molecules dissolved in solvents of different polarity. At the moment of electronic excitation the solute molecule changes its charge distribution rapidly (in about 10^{-15} s). As a result, the solute-solvent interaction forces also change. The state and solvent dependence of interaction forces leads to solvatochromic shifts in both the absorption and the fluorescence spectra. In the latter case, since the dynamic equilibrium existing prior to excitation is disturbed, a process of relaxation toward the new equilibrium configuration is accompanying the emission. Depending on the time scales of these two processes, one may observe fluorescence of an unrelaxed, relaxing, or relaxed solute-solvent system.

The solvatochromic shifts of the steady-state absorption or fluorescence spectra allow us to estimate some molecular parameters of the solute and solvent molecules. The most frequently used "classical" approach, based on continuous solvent models,^[1-4] has

been widely employed to determine solute dipole moments in the ground and excited states. The works based on the continuous solvent model were recently summarized by Suppan in his review article.^[5] The role of the dipole moments, polarizability, and other parameters was considered there. The formulae derived in the above-mentioned papers contain phenomenological parameters such as the electric permittivity and the refractive index.

Another approach was presented in the work of Macgregor and Weber.^[6] In their discussion of the behavior of the fluorescence probe Prodan in polar solvents, they assumed that every solute molecule interacts with two solvent molecules and took into account the mutual solute-solvent orientations. Their microscopic description avoids the use of the electric permittivity and the refractive index. The model seems to be rather crude but it enabled interpretation of the observed temperature "blue shift" of Prodan fluorescence in *n*-butanol.

When the experimental conditions are such that the characteristic relaxation time is comparable with the fluorescence lifetime of the solute molecule, time-dependent experiments can reveal the solvation dynamics and allow determination of the molecular parameters.^[7-10] The interpretation of these experiments may be based on

¹ Institute of Physics, Nicholas Copernicus University, Grudziądzka 5, 87-100 Toruń, Poland.

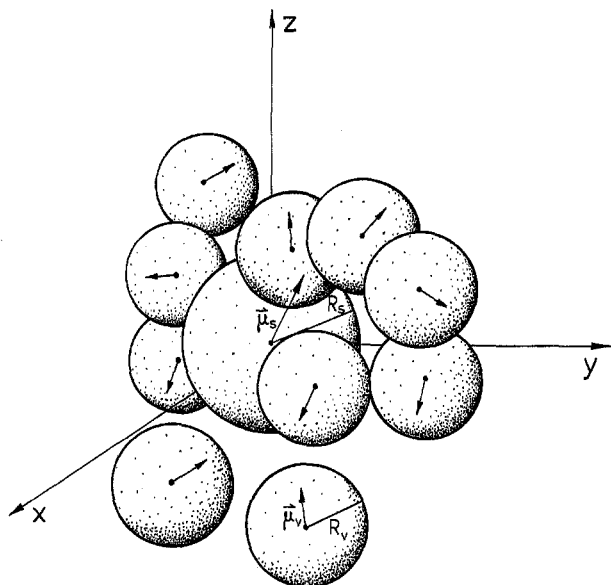


Fig. 1. Cluster consisting of a single solute molecule S and 10 solvent molecules V_s . Arrows represent dipole moments.

the extension of the continuous solvent model^[11,12] or microscopic descriptions making use of the appropriate Fokker–Planck equation.^[13]

The dipole moments and other molecular parameters can also be determined in fluorescence experiments in which the sample is under the influence of the external electric field.^[14,15] More recently, Baumann and Deckers^[16] and Liptay and Becker^[17] have significantly improved this experimental method. Time-dependent measurements in the presence of the external electric field can also be considered.^[18]

The present paper is an attempt to interpret the steady-state solvatochromic effect in terms of a simple hard-sphere microscopic model, which takes into account the molecular dipole moments and polarizabilities of both the solute and the solvent molecules. Despite of its simplicity, the proposed approach appears to reproduce correctly the experimental data obtained by the authors. One of the main features of our model which is different from the continuous dielectric approach consists of taking explicitly into account the pairwise interaction between the solvent molecules. The pairwise interaction between the solute and the individual solvent molecules is also considered.

The intermolecular electrostatic interaction energy in clusters consisting of 1 solute and several (up to 10) solvent molecules was calculated using two numerical approaches:

- (a) averaging over randomly selected configurations with the Boltzmann weighting factor and
- (b) using the standard Monte Carlo algorithm.

In contrast to the continuous dielectric model, the temperature of the system is introduced in the present work directly by the Boltzmann factor.

In method a our simulations took into account the results obtained for each drawing. This was possible because the configurational space was relatively small. Method b was chosen as a more efficient one in the case of molecules with higher values of dipole moments, due to larger values of interaction energy.

Having estimated changes of the interaction energy due to electronic transitions in solute molecules, one can determine the solvatochromic shifts in both the absorption and the emission spectra.

THE MODEL

It is assumed that a diluted solute–solvent system may be treated as a large number of clusters, each of them composed of N solvent molecules V_i ($i = 1, \dots, N$) distributed randomly around a solute molecule S (Fig. 1). The solvent molecules remaining outside each cluster constitute the thermal bath at a constant temperature T .

A laboratory reference frame with a solute molecule in its origin is assigned to each cluster and the positions of solvent molecules in it are expressed in spherical coordinates. To describe the orientations of molecules, a molecular reference frame is assigned to each molecule of the cluster. The orientation of an individual molecule is determined by a set of Euler angles $\Omega_i = (\alpha_i, \beta_i, \gamma_i)$ describing the relative orientation of the molecular frame with respect to the laboratory one ($i = 0$ for a solute molecule, $i = 1, \dots, N$ for solvent molecules).

We further assume that all our molecules may be treated as point dipoles and are polarizable. Let the charge distribution of the fluorescent solute molecule be represented by permanent dipole moments $\vec{\mu}_s^g$ in the electronic ground state and $\vec{\mu}_s^e$ in the first excited state, while the polarizability tensors are $\hat{\alpha}_s^g$ and $\hat{\alpha}_s^e$, respectively. These parameters are constant in the molecular frame. Solvent molecules are characterized by a permanent dipole moment $\vec{\mu}_v$ and a polarizability tensor $\hat{\alpha}_v$. Just as for solute molecules, they are constant in molecular reference frames of individual solvent molecules and identical for each molecule.

The proposed model neglects the individual contribution of solvent molecules remaining outside the cluster, which appears to be a realistic approximation for a disordered molecular system. Furthermore, the solvato-

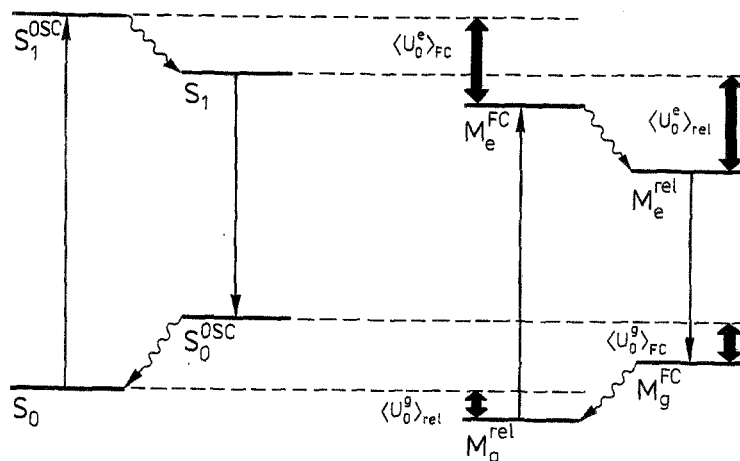


Fig. 2. The two lowest electronic energy levels of an isolated (left) and dissolved (right) molecule. S_0 and S_1 represent levels of a vibrationally relaxed isolated molecule, while S_0^{OSC} and S_1^{OSC} are vibrationally excited Franck–Condon levels. Due to the solute–solvent interaction, these levels are respectively lowered as shown on the right-hand side of the diagram. Thick arrows illustrate the solvation energies for the four levels considered.

chromic shifts are connected with solvation energy *differences* between the ground and the excited state of solute molecules, so the errors in the absolute values for individual states will tend to cancel themselves.

In considering the total interaction energy $U(\Omega)$, where $\Omega = (\Omega_0, \Omega_1, \dots, \Omega_N)$, we restrict ourselves to the electrostatic interactions for a system of permanent and induced dipole moments contained in the cluster and assume that it may be written as a sum of pairwise interaction energies,

$$U(\Omega) = \sum_{\substack{i \neq j \\ i, j=0}}^N U_{ij}(\Omega) \quad (1)$$

$U_{ij}(\Omega)$ depends on the orientation of all the molecules in a cluster, because the induced dipole moment of each molecule depends on the effective electric field at the point of its location. This field, in turn, depends on the orientation of all the molecules.

The corresponding energy of interaction between one solute and N solvent molecules is

$$U_0(\Omega) = \sum_{i=1}^N U_{0i}(\Omega) \quad (2)$$

In our model we assume that radiative electronic transitions, both absorptive and emissive, always start from a relaxed state (a state of thermodynamic equilibrium) and terminate in a Franck–Condon state. These transitions are accompanied by changes of such molecular parameters as dipole moments and polarizabilities. Thus, a process of light absorption or emission by a

solute molecule creates an orientational nonequilibrium Franck–Condon state and is followed by mutual (solute and solvent) orientational relaxation to attain a new state of equilibrium. Under the conditions of moderate exciting light intensity, the absorption is due to relaxed ground-state molecules only. In addition, when the characteristic time of orientational relaxation is short compared with the solute's excited-state lifetime, then practically all fluorescence is emitted by orientationally relaxed molecules. The latter condition is fulfilled for most organic solvents at room temperature.

In the relaxed ground state M_g^{rel} (Fig. 2), the average energy of interaction between a solute molecule and its molecular surrounding is

$$\langle U_0^g \rangle_{\text{rel}} = \frac{\int_{\Omega} d\Omega U_0^g(\Omega) \exp[-U^g(\Omega)/kT]}{\int_{\Omega} d\Omega \exp[-U^g(\Omega)/kT]} \quad (3)$$

where

$$\int d\Omega = \frac{1}{16\pi^2} \prod_{i=0}^N \int_0^{\pi} \sin \theta_i d\theta_i \int_0^{2\pi} d\phi_i \int_0^{\pi} \sin \theta_j d\theta_j \int_0^{2\pi} d\phi_j$$

We assume that spatial coordinates of molecules are fixed in a laboratory frame.

Due to the electronic excitation of the solute molecule, it finds itself in the excited Franck–Condon state M_e^{FC} . The electric dipole moment and polarizability of the solute change. At the moment of excitation the ground-state equilibrium orientations of molecules are still retained. The average interaction energy is then given by

$$\langle U_0^e \rangle_{\text{FC}} = \frac{\int_{\Omega} d\Omega U_0^e(\Omega) \exp[-U^e(\Omega)/kT]}{\int_{\Omega} d\Omega \exp[-U^e(\Omega)/kT]} \quad (4)$$

Immediately after excitation, the solute starts to relax to a new equilibrium state, M_e^{rel} , which is characterized by the interaction energy

$$\langle U_0^e \rangle_{\text{rel}} = \frac{\int_{\Omega} d\Omega U_0^e(\Omega) \exp[-U^e(\Omega)/kT]}{\int_{\Omega} d\Omega \exp[-U^e(\Omega)/kT]} \quad (5)$$

When a fluorescent solute molecule returns to the ground state, the ground-state values of its polarity and polarizability are immediately restored, but the orientations of the surrounding solvent molecules are retained. This state is denoted M_g^{FC} . Then the average energy of interaction between a solute molecule and its surrounding is

$$\langle U_0^g \rangle_{\text{FC}} = \frac{\int_{\Omega} d\Omega U_0^g(\Omega) \exp[-U^g(\Omega)/kT]}{\int_{\Omega} d\Omega \exp[-U^g(\Omega)/kT]} \quad (6)$$

The final step in the considered scheme takes place when an M_g^{FC} state relaxes to an M_g^{rel} state.

Solvatochromic shifts ΔU_{abs} and ΔU_{flu} will now be defined as differences $\langle U_0^g \rangle_{\text{FC}} - \langle U_0^g \rangle_{\text{rel}}$ and $\langle U_0^e \rangle_{\text{FC}} - \langle U_0^e \rangle_{\text{rel}}$, respectively. Thus, negative values of either ΔU_{abs} or ΔU_{flu} correspond to bathochromic shifts: positive values, to hypsochromic ones. From Eqs. (3)–(6) it follows that

$$\Delta U_{\text{abs}} = \frac{\int_{\Omega} d\Omega [U_0^g(\Omega) - U_0^g(\Omega)] \exp[-U^g(\Omega)/kT]}{\int_{\Omega} d\Omega \exp[-U^g(\Omega)/kT]} \quad (7)$$

and

$$\Delta U_{\text{flu}} = \frac{\int_{\Omega} d\Omega [U_0^e(\Omega) - U_0^e(\Omega)] \exp[-U^e(\Omega)/kT]}{\int_{\Omega} d\Omega \exp[-U^e(\Omega)/kT]} \quad (8)$$

In method a the average interaction energies given by Eqs. (3)–(6) were calculated using the following approximate expressions:

$$\langle U_0^g \rangle_{\text{rel}} = \left\{ \sum_{j=1}^M U_0^g((\Omega)_j) \exp[-U^g((\Omega)_j)/kT] / \left\{ \sum_{j=1}^M \exp[-U^g((\Omega)_j)/kT] \right\} \right\} \quad (9)$$

$$\langle U_0^e \rangle_{\text{FC}} = \left\{ \sum_{j=1}^M U_0^e((\Omega)_j) \exp[-U^e((\Omega)_j)/kT] / \left\{ \sum_{j=1}^M \exp[-U^e((\Omega)_j)/kT] \right\} \right\} \quad (10)$$

$$\langle U_0^e \rangle_{\text{rel}} = \left\{ \sum_{j=1}^M U_0^e((\Omega)_j) \exp[-U^e((\Omega)_j)/kT] / \left\{ \sum_{j=1}^M \exp[-U^e((\Omega)_j)/kT] \right\} \right\} \quad (11)$$

$$\langle U_0^g \rangle_{\text{FC}} = \left\{ \sum_{j=1}^M U_0^g((\Omega)_j) \exp[-U^g((\Omega)_j)/kT] / \left\{ \sum_{j=1}^M \exp[-U^g((\Omega)_j)/kT] \right\} \right\} \quad (12)$$

where M is the total number of steps (drawings) and $(\Omega)_j$ is a set of orientations of all the molecules in a cluster, drawn in the j th step. In method b we applied the basic Metropolis procedure.

The computational algorithm starts by choosing a random set of orientational coordinates for all the molecules concerned. The translational coordinates of solvent molecules are also randomly selected, but the choice is restricted only to those positions which exclude their spatial overlap (further details are presented in the next section). Then for each random set of translational and orientational coordinates, the total energy of the system is calculated for the ground (U^g) and excited (U^e) states of the solute as well as the solute–solvent interaction energy (U_0^g and U_0^e , respectively).

THE SOLUTE–SOLVENT INTERACTION ENERGY

Let us assume that a point solute molecule S is located at the origin of the laboratory frame and is surrounded by N solvent molecules V_i , $i = 1, \dots, N$ (Fig. 1). We ascribe effective radii R_s and R_v to the solute and the solvent molecules, respectively, which means that the minimum distance between the point dipole of the solute molecule and the point dipole of any of the solvent molecules is $R_s + R_v$, while the minimum distance between any two point dipoles representing solvent molecules is $2R_v$. No constraints are imposed on the orientational freedom of solvent molecules.

At each step of the averaging procedure, irrespective of the method used, the Euler angles of solvent molecules are chosen randomly and the translational coordinates are fixed at either $R_s + R_v$ or $R_s + 3R_v$ in such a way that solvent molecules initially fill the first spherical solvation shell and subsequently the second. For numerical reasons, the number N of solvent molecules considered did not exceed 10, which limited the number of solvent shells to 2. In our view, the above procedure allows us to model reasonably the immediate vicinity of a solute molecule, even when the number of solvent molecules in the model is small.

The effective electric dipole moment $\vec{\mu}_i$ of each molecule in a system is a sum of two components: the permanent dipole moment \vec{d}_i^{p} and the dipole moment

induced by the electric field $\vec{E}^L(i)$, generated by all the remaining molecules at a point where the i th molecule is located,

$$\vec{\mu}_i = \vec{d}_i^L + 4\Pi\epsilon_0 \hat{\alpha}_i^L E^L(i) \quad (13)$$

The superscript L refers to the laboratory frame. Any component of the permanent dipole moment in this frame, e.g., $(\vec{d}_i^L)_x$ may be expressed in terms of the molecular frame components, using the rotation matrix $R(\Omega_i)$,

$$(\vec{d}_i^L)_x = R_x^p(\Omega_i) (\vec{d}_i)_p \quad (14)$$

where $p = x, y, z$ and the Einstein summation convention is used thereafter.

The polarizability tensor $\hat{\alpha}_i$ transforms itself from the molecular to the laboratory frame as follows:

$$(\hat{\alpha}_i^L)_{xy} = R_x^r(\Omega_i) R_y^s(\Omega_i) (\hat{\alpha}_i)_{rs} \quad (15)$$

where $r, s = x, y, z$.

By inserting expressions (15) and (16) into (14) one can calculate the x component of the effective dipole moment of the i th molecule,

$$(\vec{\mu}_i)_x = (\vec{d}_i^L)_x + 4\Pi\epsilon_0 (A_i)_x^p E_p^L(i) \quad (16)$$

where

$$(A_i)_x^p = R_x^q(\Omega_i) (\hat{\alpha}_i)_{qr} R_r^p(\Omega_i) \quad (17)$$

$E_p^L(i)$ is the p th component of the electric field generated by surrounding cluster molecules at the point of location of the i th molecule and is given by the formula

$$E_p^L(i) = (4\Pi\epsilon_0)^{-1} \sum_{j \neq i}^N R_{ij}^{-3} [3(\vec{n}_{ij} \vec{\mu}_j) (\vec{n}_{ij})_p - (\vec{\mu}_j)_p] \quad (18)$$

where $R_{ij} = |\vec{R}_i - \vec{R}_j|$ and $\vec{n}_{ij} = (\vec{R}_i - \vec{R}_j)/R_{ij}$. Substituting Eq. (18) into Eq. (16) and performing simple calculations, one obtains a set of algebraic equations for components of the effective dipole moments of all the molecules in the cluster in the laboratory frame

$$(\vec{d}_i)_q = \sum_{j=0}^N [\delta_{ij} (\vec{\mu}_j)_q - (1 - \delta_{ij}) (H_{ij})_q^s (\vec{\mu}_j)_s] \quad (19)$$

where δ_{ij} is Kronecker's delta.

The term $(H_{ij})_q^s$ is defined as follows:

$$(H_{ij})_q^s = R_{ij}^{-3} [3(A_i)_q^r (\vec{n}_{ij})_r^s - (A_i)_q^s] \quad (20)$$

where $(\vec{n}_{ij})_r^s = (\vec{n}_{ij})_s (\vec{n}_{ij})_r$.

The interaction energy appearing in Eqs. (7) and (8), required to find the spectral shifts ΔU_{abs} and ΔU_{flu} , can now be calculated as

$$U_{ij} = (4\Pi\epsilon_0 R_{ij}^3)^{-1} [3(\vec{n}_{ij} \vec{\mu}_i) (\vec{n}_{ij} \vec{\mu}_j) - (\vec{\mu}_i \vec{\mu}_j)] \quad (21)$$

For a given set of random coordinates, Eqs. (19) must be solved twice: first with the solute ground-state parameters and then with those of the solute excited state. Thus obtained effective dipole moments of molecules in the cluster are then used to calculate the contribution of a given random configuration to the solvatochromic shifts.

DISCUSSION OF SIMULATION AND EXPERIMENTAL RESULTS

Numerical simulations were performed using a 386 personal computer (33-MHz CPU, arithmetic coprocessor, 64-kB cache).

Solvation energies and solvatochromic shifts were calculated for different values of molecular parameters and different temperatures. No specific molecules were considered in the first stage of our calculations (method a), which served as a consistency test of the proposed model and allowed us to make general predictions. In the second stage, we compared those predictions with experimental results obtained for coumarin 153 in four solvents (method b). The molecular ground- and excited-state dipole moments and dimensions were calculated using the INDO/S method. The values of the calculated dipole moments were consistent with those reported by Maroncelli and Fleming.¹⁹

Figure 3 presents the calculated solvation energies and solvatochromic shifts as a function of the solute excited-state dipole moment.

Practically no difference was apparent in the results when the number of solvent molecules N varied from 8 to 10. This seems to justify the assumed limit of 10 solvent molecules in a cluster. As can be seen, Fig. 3 predicts the red shift for both the absorption and the fluorescence bands on increasing the excited-state dipole moment. The effect is more pronounced in the emission.

To answer the question concerning the importance of the molecular polarizability in our model, we calculated the dependence of the solvation energy and the solvatochromic shift on the solute ground-state polarizability $\hat{\alpha}_g$ (Fig. 4). As can be seen, the polarizability significantly influences the solvation energy, while the solvatochromic shifts are relatively insensitive to it. We have also investigated the case of the anisotropic polar-

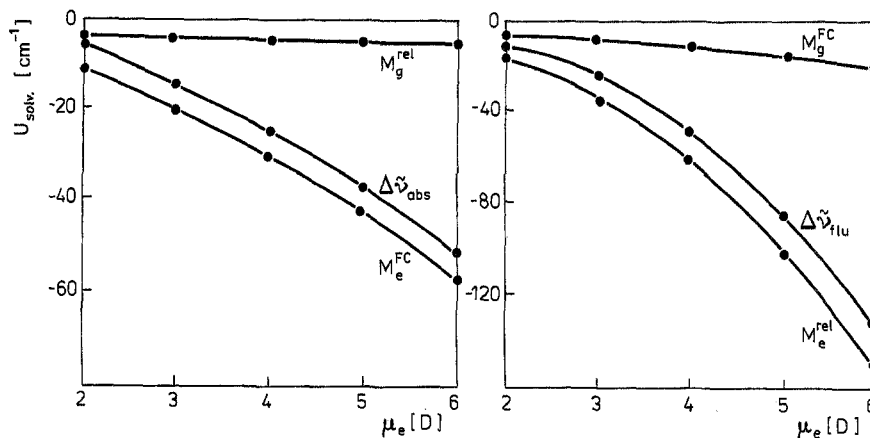


Fig. 3. Solvation energies and solvatochromic shifts as functions of the excited-state dipole moment. Solute parameters: $\mu_g = 1D$, $\vec{\mu}_e \parallel \vec{\mu}_g$, $\alpha_g = 3 \cdot 10^{-30} \text{ m}^3$, $\alpha_e = 6 \cdot 10^{-30} \text{ m}^3$, and $R_s = 0.47 \text{ nm}$. Solvent parameters: $\mu_v = 1.5D$, $\alpha_v = 5 \cdot 10^{-30} \text{ m}^3$, and $R_v = 0.38 \text{ nm}$. Temperature of the system $T = 280 \text{ K}$.

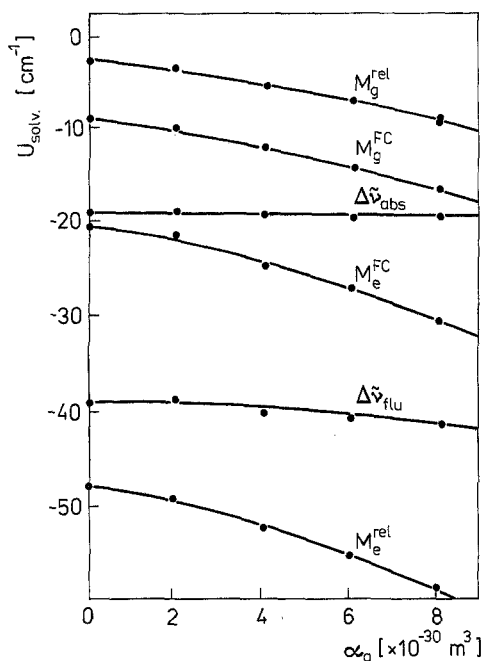


Fig. 4. Solvation energies and solvatochromic shifts as functions of the ground-state polarizability. Solute parameters: $\mu_g = 1D$, $\mu_e = 4D$, $\vec{\mu}_e \parallel \vec{\mu}_g$, $\alpha_e = \alpha_g + 4 \cdot 10^{-30} \text{ m}^3$, and $R_s = 0.47 \text{ nm}$. Solvent parameters: $\mu_v = 1.5D$, $\alpha_v = 3 \cdot 10^{-30} \text{ m}^3$, and $R_v = 0.38 \text{ nm}$. Temperature of the system $T = 280 \text{ K}$.

izability.^[19] We found that the anisotropy of $\hat{\alpha}$'s influences the solvation energy relatively weakly. Therefore this matter is not discussed further.

We have also calculated the dependence of the solvation energies and the solvatochromic shifts on the angle ϕ between the dipole moments of the ground ($\vec{\mu}_g$)

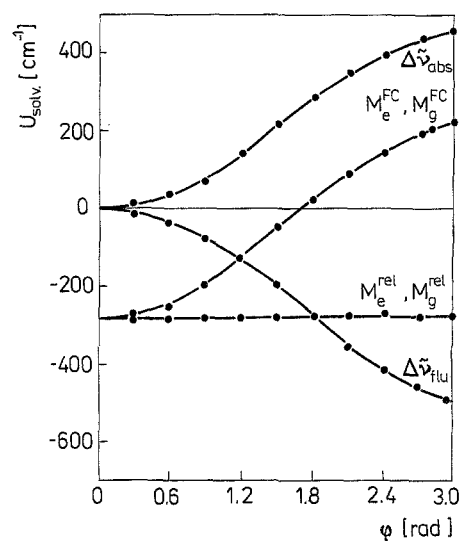


Fig. 5. The role of angle ϕ between ground- and excited-state dipole moments. The case of $\mu_g = \mu_e$. Solute parameters: $\mu_g = \mu_e = 4D$, $\alpha_g = \alpha_e = 0 \text{ m}^3$, and $R = 0.47 \text{ nm}$. Solvent parameters: $\mu_v = 1.5D$, $\alpha_v = 6 \cdot 10^{-30} \text{ m}^3$, and $R_v = 0.38 \text{ nm}$. Temperature of the system $T = 280 \text{ K}$.

and the excited ($\vec{\mu}_e$) state (Fig. 5). We have considered here the case of equal magnitude of the two dipole moments, and therefore the solvation energies of both relaxed states M_e^{rel} and M_g^{rel} are equal and angle independent. For the same reason the angle dependence of the solvation energy of M_e^{FC} and M_g^{FC} levels is identical. As a result, we obtain a blue spectral shift for the absorption and a red shift for the emission.

Additionally, we have considered the case in which also the dipole moment changes on excitation of the sol-

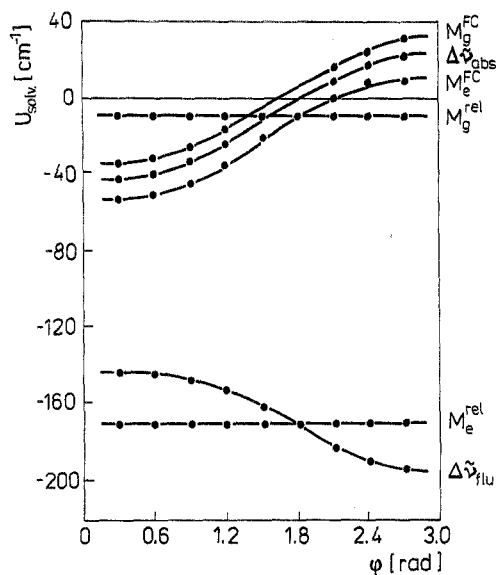


Fig. 6. The role of angle ϕ between ground- and excited-state dipole moments. The case of $\mu_g < \mu_e$, $\mu_g = 1D$. The remaining parameters are as for Fig. 5.

ute molecule. Figure 6 was obtained for the set of parameters differing only by the value of μ_g , which was assumed here to be $\vec{\mu}_g = (1,0,0)[D]$. In contrast with Fig. 5, the solvation energies of M_g^{rel} and M_e^{rel} are different here. Figure 6 also demonstrates that the lack of solvatochromic shift in the absorption does not necessarily mean that the solute molecule is nonpolar, since at a certain value of the angle between $\vec{\mu}_g$ and $\vec{\mu}_e$, the influence of its polarity vanishes.

The model introduced in this work can also be applied to studies of thermochromic spectral shifts. We now discuss the results of Monte Carlo simulations (method b) and compare them with the experimentally determined thermochromic shifts for coumarin 153 in four solvents (chlorobenzene, chloroform, pyridine, and methanol). The molecular parameters used in Monte Carlo simulations were derived from quantum-chemical calculations using the INDO/S method. The following values were obtained: $\mu_g = 5.97 D$, $\mu_e = 9.43 D$, and $\cos\phi = 0.98$. The maximum molecular dimension h was estimated to be 0.98 nm for coumarin 153, 0.29 nm for chloroform, 0.27 nm for methanol, 0.49 for pyridine, and 0.56 for chlorobenzene. The effective radii R_g and R_e used in our simulations were initially taken as one-half of the above values, but we found that the best agreement with the measured thermochromic shifts is obtained when a reduction factor of 0.8 is introduced. The polarizability of the solute and the solvent molecules

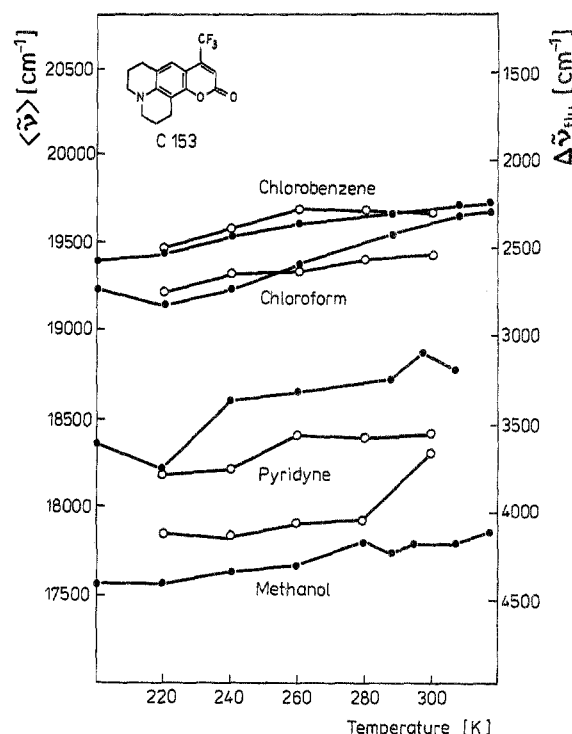


Fig. 7. Comparison between experimental and simulated thermochromic shifts for coumarin 153. Filled circles depict the mean wavenumbers ($\bar{\nu}$) of the measured fluorescence spectra. Open circles correspond to the calculated thermochromic shifts $\Delta\bar{\nu}_{\text{flu}}$.

was neglected, which appears to be justified in view of the preceding discussion (and the lack of such data).

The measured thermochromic shifts are compared with the simulation results in Fig. 7. The vertical axis on the left-hand side refers to the mean wavenumber ($\bar{\nu}$) of the fluorescence band calculated as an arithmetic mean of the two half-maximum values. The vertical axis on the right-hand side refers to the thermochromic shifts calculated for the fluorescence. The shifts are expressed relative to the ($\bar{\nu}$) value of 21,960 cm^{-1} , corresponding to a "noninteracting" solvent. It should be mentioned here that for coumarin 153 in cyclohexane, the experimentally determined mean fluorescence wavenumber averaged over the temperature range of 288–318 K is about 21,800 cm^{-1} . In Fig. 7 one can notice the temperature blue-shift of fluorescence for both the experimental and the simulated results.

The necessity of introducing a dimensional reduction factor of 0.8 in our calculations indicates that the molecules considered cannot be treated as spherically symmetrical and may approach each other more closely than would result from adding their effective radii taken as $1/2h$.

To summarize, we would like to draw the reader's attention to the following features of the proposed description.

- (1) It yields results which can be directly compared with the experiment.
- (2) It has an advantage of taking explicitly into account the temperature as a parameter.
- (3) It can be easily modified for various interaction potentials, to include the nondipolar interactions, in particular the hydrogen bonding in protic solvents,
- (4) Its simplicity allows to performance of the calculations using relatively small computing powers.

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