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ARTICLES

Stokes Shift as a Tool for Probing the Solvent Reorganization Energy

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The difference between the maxima of absorption and fluorescence spectra, the Stokes shift, is affected by dynamic properties of the solvent, namely by the solvent reorganization free energy, E_s. Stokes shift a dye, proflavine, in polar aprotic solvents and in alcohols is examined. We report that the experimentally observed dependence of E_s on the solvent dielectric properties can be explained only when two effects are taken into account. The first effect is the distortion of dielectric properties of a uniform solvent by embedding a bulk solute molecule in the solvent. The second effect is the influence of the solvent polarity on the electronic density redistribution upon the electronic transition. Our model evaluations of E_s are based on quantum chemical calculations of solvent effects on charge redistribution of the dye upon excitation and on subsequent calculations of E_s in the framework of a model of a cavity in a continuum dielectric. We show that the continuum approach is able in the present case to provide a reasonable correlation between E_s and the dielectric properties of the solvent. An experimentally observed 15%−30% difference in the values of E_s for polar aprotic solvents and for alcohols cannot be explained in terms of the continuum approach. Our data show that commonly adopted equation for Stokes shift that establishes equality between Stokes shift and the doubled reorganization energy is generally not rigorous. The experimental data obtained are consistent with a more rigorous approximation of Stokes shift that takes into account the quantum nature of the solute local modes.

1. Introduction

Charge transfer processes are strongly affected by the dielectric properties of the polar environment. The charge (electronic density) redistribution upon light absorption or emission also belongs to this class of processes. Fast rearrangement of the solute electronic density upon transition between electronic states takes place at a fixed configuration of both the solute nuclei and the slow inertial polarization of the surroundings. After the transition, the solute nuclei and the inertial polarization relax from the configuration existing in the equilibrium initial electronic state, which is a nonequilibrium one for the final electronic state, to the new equilibrium positions. The free energy change associated with such a relaxation process is known as the reorganization free energy. The reorganization energy depends on dynamic dielectric properties of the environment.

The role of the dynamic dielectric properties in charge transfer reactions was recognized first by Marcus,[1] while their role in light absorption or emission processes was understood first by Lippert[2,3] and Mataga et al.[4,5] and later by Marcus[6] and Hush.[7] Further development of the theory of photoinduced charge transfer transitions[8−10] made it possible to relate the spectral band shape to the frequencies of normal modes and the displacements of normal coordinates of the solute and to the dielectric properties of the environment.

For transition between the same two electronic states, the absorption and emission band maxima, ν_a and ν_f, are approximated by relations[6−8,10]

$$h\nu_a = \Delta F_0 + E_r, \quad h\nu_f = \Delta F_0 - E_r \tag{1}$$

where h is Plank's constant, E_r is the reorganization free energy, and ΔF_0 is the equilibrium free energy gap between the ground and excited states. Linear combinations of these equations give

$$h\nu_a - h\nu_f = 2E_r, \quad h\nu_a + h\nu_f = 2\Delta F_0 \tag{2}$$

The first of these relations determines the Stokes shift of fluorescence that is affected by nonequilibrium dielectric properties. The quantity determined by the second relation is influenced by equilibrium properties of the environment. Relations 2 establish the basis for the methods of experimental study of both the static and dynamic dielectric properties of polar media. In the next section we discuss a more precise approximation of the absorption and emission band maxima.

When the solute normal coordinates change at the transition, this also contributes to E_r. If the entangling of solute and solvent normal coordinates may be neglected, E_r is[8−10]

$$E_r = E_{is} + E_s \tag{3}$$

where E_{is} is the inner sphere reorganization energy owing to solute local modes and E_s is the outer sphere (solvent) reorganization free energy due only to solvent modes.

A powerful tool in charge transfer theories is the continuum description of the environment. If the charge transfer occurs between two separated spherical particles immersed in a

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dielectrically uniform medium, E_s is proportional to the coupling parameter C of the medium[1]

$$E_s = e^2C(1/2a_1 + 1/2a_2 - 1/R), \quad C = 1/\epsilon_{op} - 1/\epsilon_{st} \quad (4)$$

where ϵ_{op} and ϵ_{st} are the optical and static dielectric constants of the solvent, a_1 and a_2 are the radii of the two reactants, and R is the distance between them.

If the charge transfer takes place inside a bulk solute (or between two reagents close to each other), the solute by itself produces a dielectric inhomogeneity in a uniform solvent. This case is usually approached by dielectric cavity model that describes the solute as a cavity of a definite shape formed in a uniform dielectric. This model was first employed for calculation of Stokes shift by Lippert[2,3] and Mataga et al.[4,5] They approximated a chromophore by a spherical cavity of radius a with a point dipole at its center, the value and the direction of the dipole being changed by $\Delta\mu$ upon photoinduced transition. In that model, in the present notion, E_s is

$$E_s = \frac{(\Delta\mu)^2}{a^3}\left(\frac{\epsilon_{st}-1}{2\epsilon_{st}+1} - \frac{\epsilon_{op}-1}{2\epsilon_{op}+1}\right) = \frac{(\Delta\mu)^2}{a^3}\frac{3}{4}\left(\frac{1}{\epsilon_{op}+{}^1/_2} - \frac{1}{\epsilon_{st}+{}^1/_2}\right) \quad (5)$$

Another general approach to calculation of E_s for the case of an arbitrary charge distribution inside a nonuniform dielectric adopted until recently[11] predicted E_s to be proportional, similar to eq 4, to the coupling parameter of the solvent and a geometrical factor, which, generally, weakly depends on the static dielectric constant of the surrounding (see for reviews refs 12 and 13).

In accordance with the above considerations, it was found in several works that in many case the Stokes shift of various chromophores in solvents and their mixtures correlates, to a degree, with Lippert's parameter (term in brackets of eq 5)[3,5,14−17] or with coupling parameter C.[18,19]

The purpose of this work is to investigate relations between the solvent reorganization energy and the dielectric properties of the solvent with the aid of Stokes shift. We will analyze whether correlation between the reorganization energy and Lippert's or coupling parameters of the solvent generally takes place for the charge redistribution upon electron transition occurring inside the cavity. We discuss that, even in the case when E_s obeys formally eq 4 or 5, the geometrical factor of charge transfer or the difference of the dipole moments in the ground and excited states can not be correctly extracted from the data only on absorption and/or emission maxima of real chromophores.

We report also a correlation between experimental data on Stokes shift of dicationic dye proflavine in various solvents and their mixtures and semiquantitative theoretical estimates of it. These estimates are based on quantum chemical calculations of these dye and on subsequent calculations of E_s using the cavity model recently developed.[20]

2. Relation between Stokes Shift and Dielectric Properties of the Surroundings

Usually, electronic transitions are coupled with the change of vibrational state of the molecule (vibrational quantum number). Therefore, the electronic spectrum of chromophores has vibrational structure, and the band shape function of chromophores (which differs from the observed spectra by a factor of the light frequency to an integer power) is generally asymmetric. In the case of an asymmetric band, relations 1 are valid only to the first approximation. In our recent work[21] a more precise estimate of the maximum of a structureless band shape function with a single maximum was obtained:

$$h\nu_a = \Delta F_0 + E_{ra} - M_{3a}/2M_{2a}, \quad h\nu_f = \Delta F_0 - E_{rf} - M_{3f}/2M_{2f}, \quad \text{and, } h\nu_a - h\nu_f = (E_{ra} + E_{rf}) - {}^1/_2(M_{3a}/M_{2a} - M_{3f}/M_{2f}), \quad h\nu_a + h\nu_f = 2\Delta F_0 + (E_{ra} - E_{rf}) - {}^1/_2(M_{3a}/M_{2a} + M_{3f}/M_{2f}) \approx 2\Delta F_0 \quad (6)$$

Here, ν_a and ν_f are the maxima of the absorption and fluorescence band shape functions and M_2 and M_3 are the second and third central momenta of the band shape function, $S(\nu)$

$$M_n \equiv \int_{-\infty}^{+\infty} (\nu - m_1)^n S(\nu)\, d\nu, \quad m_1 \equiv \int_{-\infty}^{+\infty} \nu S(\nu)\, d\nu \quad (7)$$

These estimates (eq 6) were derived from the approximation of the band shape function within its half-width (half the width on the half-height) around the maximum

$$S_k(\nu) \sim (1 + \alpha_k(\nu - \nu_k)^3/M_{2k}^{3/2}) \exp(-(\nu - \nu_k)^2/2M_{2k})$$
$$\alpha_k \equiv M_{3k}/6M_{2k}^{3/2} \ll 1, \quad k = a, f \quad (8)$$

which is valid when the coefficients α_k are small. Note that M_2 is always positive and M_3, and thus α, is positive (negative) for the absorption (emission) spectra.[21] The subscripts a and f at E_r and the momenta allow for some possible difference in the intramolecular normal mode frequencies in the ground and excited states.[22]

When the entangling of the solute and solvent modes is negligible, the central momenta are the sums of the terms due to either the solvent or the solute. As to the contribution of the solvent to the momenta, one can usually neglect the influence of the quantum modes of a polar solvent because their contribution to the spectrum of dielectric losses at room temperature is weak. To a good approximation, one can set $M_2 \approx M_{2is} + 2kTE_s$ and $M_3 \approx M_{3is}$. From these considerations it follows that the dependence of the Stokes shift on E_s assumes a nonlinear form[21]

$${}^1/_2(h\nu_a - h\nu_f) = E_s + E_{is} - {}^1/_4(M_{3a}/M_{2a} - M_{3f}/M_{2f}) \approx E_s + E_{is} - \frac{1}{4}\left[\frac{M_{3isa}}{(M_{2isa} + 2kTE_s)} + \frac{|M_{3isf}|}{(M_{2isf} + 2kTE_s)}\right], \quad E_{is} \equiv {}^1/_2(E_{isa} + E_{isf}) \quad (9)$$

where M_{2is} and M_{3is} are the second and the third momenta of the band shape function due to the solute local modes (which are independent of E_s), k is the Boltzmann constant, and T is the temperature.

The main reason of the appearance of the last term in eq 9 is the asymmetry of the band shape. Because the strong spectrum asymmetry is an intrinsic property of usual chromophores with quantum modes, this term is important. Its value may attain a substantial part (*e.g.*, up to a half) of the observed Stokes shift.[21]

Equations 1 and 2 and a more rigorous eq 9 were derived using some assumptions that hold true at certain conditions. To study experimentally the solvent reorganization energy with the aid of the Stokes shift defined by relation (eq 9), the following conditions must be met:

(1) The emission must occur from the same electronic state to which the solute was excited, so that the solvent reorganiza-

tion energy and the free energy gap between the ground and excited states will be the same for the absorption and emission processes.

(2) The ground and excited states must be the same in the set of solvents used. The closely related requirement is the absence of the degeneracy of both electronic states in order to avoid the overlapping of the spectra due to different electronic transitions.

(3) The solute must not undergo a photoinduced conformational transition upon excitation. Upon such a photoinduced transition, the movement along the intramolecular modes associated with the transformation is followed by substantial change of the whole shape of the solute, and thus the shape of the cavity, which results in a strong coupling between these modes and the solvent polarization. As a consequence, the separation of the total reorganization energy on the two independent components (eq 3) fails.

(4) The solute normal modes and their parameters must be the same in the set of solvents used in order to isolate the environment effects only on the solvent reorganization energy.

(5) The charge redistribution function due to the electronic transition should be the same in the set of solvents used.

(6) For the theory of charge transfer based on Born–Oppenheimer approximation to hold, the characteristic frequency of the electronic transition should be greater than the frequency of the solvent inertial polarization and lower than that of its electronic polarization. This condition is generally met when the solute electronic spectrum lies in the transparency region of the solvent.

(7) Practically all excited solute molecules should emit light when all relaxation processes are completed; *i.e.*, the lifetime of the excited state is greater than the time of the longest relaxation process. The longest process is usually the orientational relaxation of the solvent molecules.

(8) Both the absorption and emission bands should be structureless bands with a single maximum in all solvents used.

To correlate the Stokes shift with the dielectric properties of the environment, one should assume the relationships between E_s and the properties of the solvent. The general theory of charge transfer relates E_s with the dielectric losses spectrum of the solvent (see, *e.g.*, ref 23). For a case of uniform solvent this relation may be reduced to proportionality to the coupling parameter (eq 4). A large solute–solvent system is inhomogeneous. It was recently shown[24–26] that the approach[11] used so far for the calculation of E_s in nonuniform medium is invalid and may result in not only quantitatively but also qualitatively incorrect results.[20,24]

Generally, the solvent reorganization energy must be calculated[24,25] as the difference of the electrostatic free energies of the effective charge distribution (defined as the change of charge distribution function upon a transition) in a real dielectric medium and in the fictitious dielectric with the permittivity equal to the optical dielectric constant of the real dielectric. This protocol, unlike that of ref 11, does not predict that E_s of the charge transfer inside a cavity is proportional to the coupling parameter: a particular form of the dependence of E_s on the dielectric constants of the solvent is rather complex and is a function of the cavity shape.[20] Therefore, the analysis of the correlations between E_s and the dielectric properties of the solvent observed experimentally can be performed only in conjunction with theoretical estimates of E_s for a particular system.

3. Results and Discussion

As a probe, dicationic dye proflavine (PF), was chosen. Its long-wave absorption and the corresponding emission bands that are transitions between the ground and the lowest excited singlet states were studied (for experimental details, see section 5). First of all, we tested the conditions given in section 2 for a dye to serve as a probing tool.

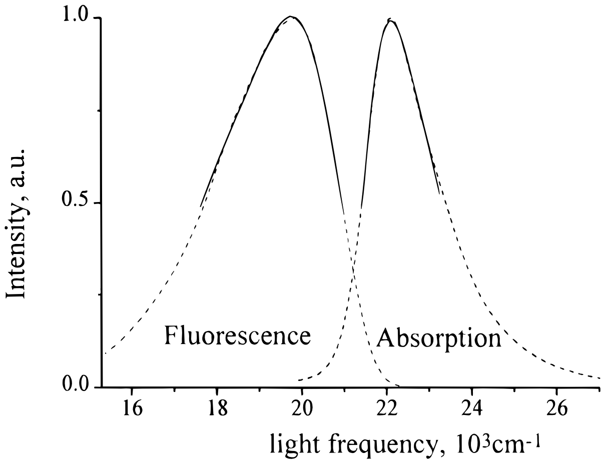


Figure 1. Absorption and fluorescence band shape functions of dicationic dye proflavine solution in acetonitrile (dashed curves). Band shape functions were obtained by dividing absorption and corrected fluorescence spectra by the frequency to the first and fifth powers, respectively. Solid curves show the result of the least-squares fitting of eq 8 to the data and the typical ranges of the data used for fitting.

Features of the Long-Wave Transition of the Dye. PF is a plane rigid molecule, and we do not expect a photoinduced transition upon excitation (condition 3). Mirror symmetry of absorption and fluorescence spectra of PF observed in all solutions studied (see Figure 1) suggests that conditions 1, 2, and 3 are fulfilled. Both the absorption and emission bands lie in the visible region and, therefore, in the transparency region of usual solvents (condition 6). We also have found that the fluorescence polarization of PF in glycerol solution, where fast rotational depolarization of fluorescence is prevented due to high viscosity, is the same within the long-wave absorption band (that is, polarization is independent of the excitation wavelength). Hence, the absorption occurs on the same electronic level from which the dye emits,[27] and this is additional evidence that condition 1 is met.

The quantum yield of the fluorescence of PF is about 0.36.[28] Having calculated the integral intensity of absorption band of the dye, we estimated (according to ref 29, using the relation between the quantum yield, the integral intensity, and the lifetime) the lifetime of the excited state to be about 1 ns. This time is much greater than the time of longitudinal relaxation in usual solvents. Adding the dynamic quencher of PF fluorescence, potassium iodide, in acetonitrile, and decreasing thereby the quantum yield and, thus, the lifetime by up to 15 times, we found that the position and the shape of the fluorescence band do not change. Thus, we conclude that the fluorescence predominantly takes place when all relaxation processes are completed (condition 7).

We have found that the position and shape of the fluorescence spectrum are independent of the wavelength of excitation, providing the dye is excited within the long-wave absorption band. This means that the relaxation started from any point on the energy surface is completed before the emission process (condition 7) and that there is no overlapping of electronic transitions within the absorption and emission bands under study (conditions 1, 2). From the above observation we also conclude that in the solutions employed there were no impurities fluorescing in the visible range.

In all solutions studied the long-wave absorption and fluorescence bands are structureless and have a single maximum.

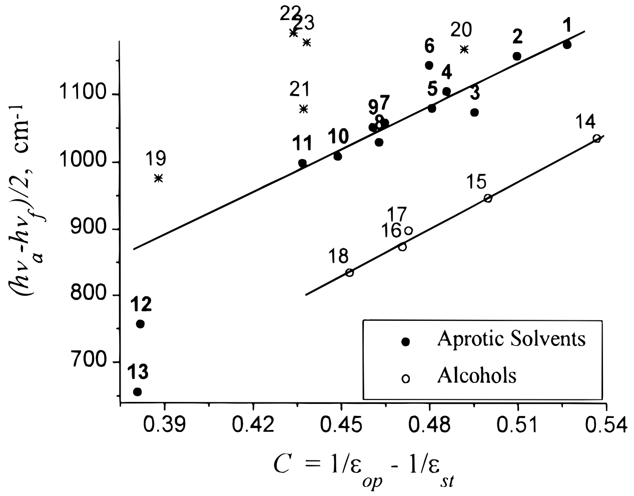


Figure 2. Half of the Stokes shift of fluorescence of proflavine solutions $^1/_2(h\nu_a - h\nu_f)$ plotted versus the coupling parameter C of a solvent. The following liquids were used as the solvent: ***1***, acetonitrile; ***2***, γ-butyrolactone (25 vol %)−acetonitrile mixture; ***3***, acetone; ***4***, propylene carbonate (62%)−acetone mixture; ***5***, acetonitrile (32%)−γ-butyrolactone mixture; ***6***, propylene carbonate; ***7***, γ-butyrolactone (86%)−acetone mixture; ***8***, *N*,*N*-dimethylformamide; ***9***, γ-butyrolactone; ***10***, dimethyl sulfoxide (77%)−acetone mixture; ***11***, dimethyl sulfoxide; ***12***, 1,2-dichloroethane; ***13***, dichloromethane; ***14***, methanol; ***15***, ethanol; ***16***, 1-propanol; ***17***, 2-propanol; ***18***, 1-butanol; ***19***, benzonitrile; ***20***, acetonitrile (50%)−*N*,*N*-dimethylformamide mixture; ***21***, 1,4-dioxane (10%)−γ-butyrolactone mixture; ***22***, acetonitrile (35%)−1,2-dichloroethane mixture; ***23***, acetone (50%)−1,2-dichloroethane mixture.

Only in solvents with the lowest reorganization energy, dichloroethane and dichloromethane, a slight hint on the existence of a shoulder on the high-frequency side of long-wave absorption band can be discerned. Therefore, condition 8 is usually met.

So, we may use proflavine to study correlations between E_s and the dielectric properties of the environment. (Conditions 4 and 5 that have not been considered here will be tested below.)

Stokes Shift of the Dye. Equation 9 predicts that Stokes shift is a monotonous single-valued function of the solent reorganization energy. If E_s is a linear function of, say, the coupling parameter, Stokes shift is also monotonous function of the latter. Let us find out whether this is the case. Plotted in Figure 2 is the Stokes shift of PF versus the coupling parameter of the solvent. (The dielectric constants of solvents and their mixtures were taken from refs 30 and 31. The constants of mixtures that are not available in ref 31 were calculated from the constants of pure solvents with the aid of the Clausius−Mossoti equation.[31])

Let us consider first the data for individual solvents and some mixtures numbered from 1 to 18. All points for alcohols (14−18) lie on the straight line (fitting open circles). This seems consistent with the assumption of a linear relation between E_s and C. The data for polar aprotic solvents and some mixtures of solvents (1−13) are marked by closed circles. (Some cases of media with specific solvation properties, marked by asterisks, *viz.* points 19−23, will be discussed at the end of this section.) The static dielectric constant of medium for most of these points is virtually the same (in the range of 37−45), and they fit the other straight line. The four points that drop out from the line, *i.e.*, propylene carbonate (6), acetone (3), dichloroethane (12), and dichloromethane (13), have a considerably different ϵ_{st} of 65, 21, 10, and 9, respectively. The slopes of the lines for alcohols and polar aprotic solvents are different. The plot of Stokes shift versus Lippert's parameter (not shown) turned out to be quite similar to that in Figure 2. So, there is no monotonous unique dependence of Stokes shift on either Lippert's or coupling parameters.

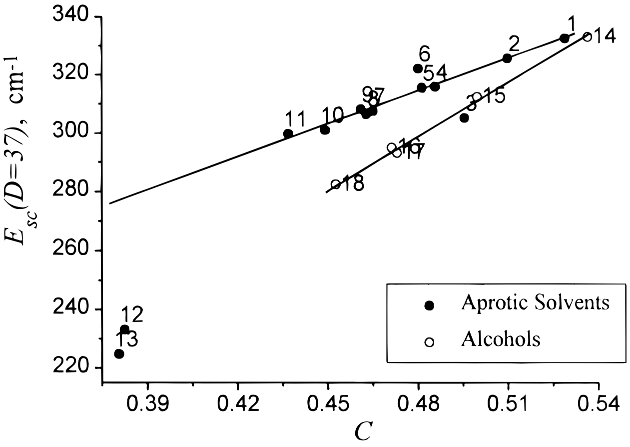


Figure 3. Calculated value of the solvent reorganization energy E_{sc} (D=37) for the transition between the ground and the lowest excited states of proflavine plotted versus the coupling parameter. The charge redistribution function was obtained from quantum chemical calculations of the dye in a dielectric with the permittivity $D = 37$. For all points the charge redistribution was the same. The optical and static dielectric constants used in calculating $E_{sc}(D{=}37)$ for the given charge redistribution were the same as the constants of solvents studied experimentally. Numbering of the points is the same as in Figure 2.

Quite similar deviations of the points for polar aprotic solvents with different ϵ_{st} were observed in some other spectroscopic studies. For instance, the deviations were found for the dependence of Stokes shift of 1-aminonaphthalene[14] and PRODAN[17] in aprotic solvents on Lippert's parameter, the dependence of solvent reorganization energy of betaine-26 (extracted from the band shape analysis) on the coupling parameter,[32] and the dependence of charge transfer band maximum of biferrocene monocation on the coupling parameter.[33] In the latter work the deviation for dichloromethane from a set of another polar aprotic solvent with considerably greater static dielectric constant was attributed to the effect of dielectric saturation. In the other works cited here the analysis of the deviations within the group of aprotic solvents was not given.

We suggest that the same physical effects may underlie the deviations reported in the papers quoted above and in the present study. The absence of a monotonous dependence of E_s on either Lippert's or coupling parameters may be caused by the reason that, for a dielectrically inhomogeneous medium, the solvent reorganization energy is not proportional to either of the two parameters.

Relation between the Solvent Reorganization Energy and the Dielectric Constants of the Solvent. According to the modern theory of charge transfer reactions,[24,25] the dependence of E_s on the dielectric constants of the solvent is rather complex. Figure 3 shows that the coupling or Lippert's parameters cannot approximate this dependence. In this figure, the reorganization energy $E_{sc}(D = 37)$ was calculated for a charge redistribution of PF for the electronic transition between the ground and the lowest excited states using the model of an oblate spheroid dielectric cavity (hereafter, all calculated values of E_s are specified by a subscript c). This charge redistribution was *the same* for all points and was obtained from quantum chemical calculations of the dye surrounded by a dielectric with the permittivity $D = 37$ (see section 6 and the text of the subsection below). The plot of $E_{sc}(D = 37)$ versus Lippert's parameter (not shown) turned out to be quite similar. This was expected from the resemblance of the coupling and Lippert's parameters as functions of the dielectric constants (compare eqs 4 and 5).

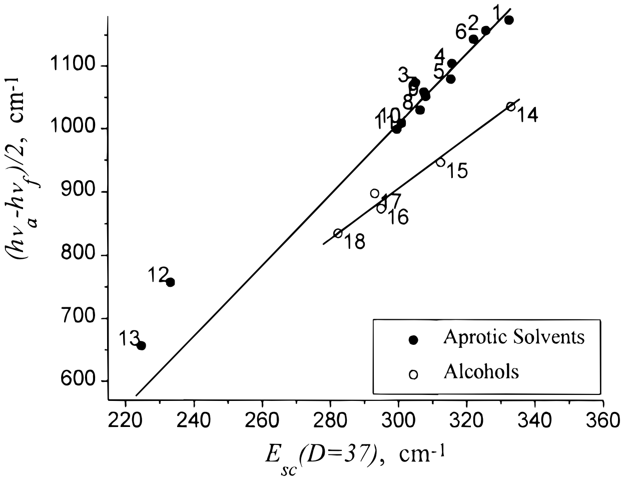


Figure 4. Half of the Stokes shift of fluorescence of proflavine solutions $^1/_2(h\nu_a - h\nu_f)$ plotted versus the calculated value of the solvent reorganization energy $E_{sc}(D{=}37)$ taking into account only the effect of inhomogeneity produced by a bulk solute molecule in a uniform solvent. The charge redistribution function was the same for all points, and it was obtained from quantum chemical calculations of the dye in a dielectric with the permittivity $D = 37$. The optical and static dielectric constants used in calculating $E_{sc}(D{=}37)$ for the given charge redistribution were the same as the constants of solvents studied experimentally. Numbering of the points is the same as in Figure 2.

One can see that Figures 2 and 3 are qualitatively similar: the points for media with close static dielectric constants lie on the same straight line; the points for solvents of strongly different ϵ_s (points 3, 6, 12, 13) deviate in the same manner as in the experimental set of data; the slope of the line for alcohols is larger than that for aprotic solvents. Thus, we conclude that the effect of the dielectric cavity on the solvent reorganization energy causes the deviations of E_s of the type experimentally observed.

However, this effect is not sufficient to explain quantitatively the present experimental data. Despite the better (than in Figure 2) correlation between the observed Stokes shift and the calculated reorganization energy $E_{sc}(D = 37)$ (Figure 4), some discrepancy between the data and the calculations still occurs: points 3, 12, and 13 with different ϵ_{st} deviate from the straight line for polar aprotic solvents (closed circles); there is a gap between the lines for polar aprotic solvents and for alcohols (open circles); the slopes of the two lines are different.

Conditions 4 and 5 have not been tested so far. In the set of alcohols used, ϵ_{st} is not constant and decreases systematically in parallel with decreasing C. This circumstance and the deviations of the points (with different ϵ_{st}) in the set of polar aprotic solvents suggest that either the parameters of the solute local modes or the charge redistribution function depends on the permittivity of the solvent. Let us turn first to testing the last explanation.

Relation between the Charge Redistribution Function of the Dye and the Medium Dielectric Permittivity. We analyzed the influence of the surroundings dielectric permittivity D on the dye charge redistribution. We performed quantum chemical semiempirical (PM3) calculations of PF in the self-consistent equilibrium reaction field of surroundings having various D's (for all details we refer to section 6) and found that the charge redistribution decreases with increasing D (Table 1). For the charge redistributions given in Table 1, the solvent reorganization energies calculated for the same model solvent (having $\epsilon_{st} = 37$ and $\epsilon_{op} = 2$) differ by 1.5 times (the value being higher at $D = 1$).

TABLE 1: Change of Effective Partial Charges (in electron charge *e*) of Proflavine Atoms Representing the Charge Redistribution Function Obtained from Quantum Chemical Calculations of the Dye in Gaseous ($D = 1$) and Aqueous ($D = 80$) Surroundings[a]

atom	$D = 1$	$D = 80$
1	+0.073	+0.073
2	+0.010	+0.020
3	+0.060	+0.018
4	+0.036	+0.018
5	−0.106	−0.080
6	−0.030	−0.041
7	−0.021	−0.012
8	+0.029	+0.079

[a] Numbering of the dye atoms is shown in Scheme 1. Symmetrical atoms are omitted.

The electronic density distribution influences the parameters of normal vibrational modes of the solute. Hence, the parameters of modes of our chromophore are, in principle, also affected by the surrounding permittivity D. However, for the rigid PF molecule, the intramolecular parts of the reorganization energy and the momenta are determined predominantly by the "rigid" high-frequency (of the order of 1000 cm^{-1}) vibrational modes[21] that are less affected by the changes in the surroundings reaction field. Indeed, we found from our data that M_3, which is practically not affected by the solvent modes,[21] is the same within the experimental errors for the solvents with different permittivity (within each solvent group). Thus, we can conclude that the influence of dielectric surrounding on the solute vibrational modes does not play a substantial role.

Values of E_{sc} Calculated Combining Quantum Chemical Data with Cavity Model Calculations. To include both the solvent effect on solute electronic properties and the effect of the system's dielectric inhomogeneity, we calculated the solvent reorganization energy E_{sc} in the framework of the cavity model using the charge redistribution obtained from quantum chemical calculations with the parameter D equal to the static dielectric constant of a given solvent, $D = \epsilon_{st}$. The plot of the observed value of Stokes shift (Figure 5) versus model estimate of the solvent reorganization energy (E_{sc}) demonstrates a good linear dependence for both sets of solvents. The points dropped out from the line for polar aprotic solvents in Figure 2, together with the other points from this set of solvents (except point 12), lie on the same line. The deviation of Stokes shift in dichloroethane (point 12) from the value predicted from the linear dependence in Figure 5 (closed circles) is relatively small, about 60 cm^{-1}. This deviation can be attributed to specific properties of the solvent (see the end of this section).

Thus, one can attain a good correlation between the experimental data on Stokes shift and calculations taking into account simultaneously the effect of dielectric inhomogeneity and the solvent effect on the charge redistribution.

Absolute Values of the Solvent Reorganization Energy. As it was discussed in our previous paper,[21] given the data on the Stokes shift and the momenta, one can obtain only the total reorganization energy $E_r = E_s + E_{is}$ (eq 9). To find the true values of the solvent reorganization energies, the relation between E_s and the dielectric properties of the solvent should be known. In our analysis, we assume that these properties can be represented by some integral parameter, namely the calculated solvent reorganization energy E_{sc}. We suppose that the true value of the solvent reorganization energy E_s and the calculated one E_{sc} are related by some scaling factor p

$$E_s = pE_{sc} \tag{10}$$

The values of p were found from the slopes of the lines in Figure

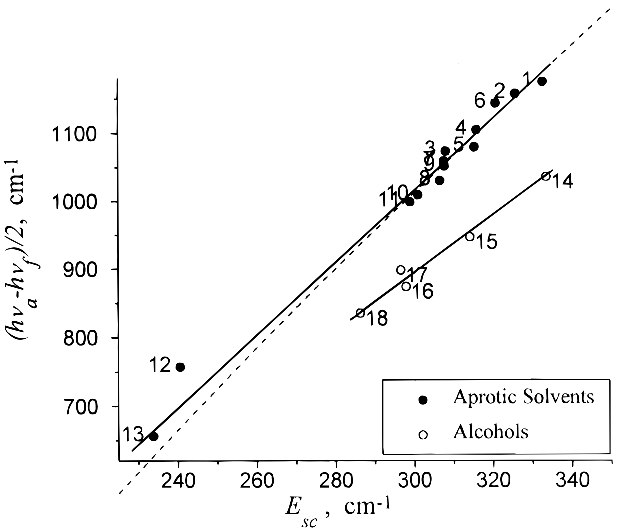


Figure 5. Half of the Stokes shift of fluorescence of proflavine solutions $^1/_2(h\nu_a - h\nu_f)$ plotted versus the calculated value of the solvent reorganization energy E_{sc} taking into account both the effect of inhomogeneity produced by a bulk solute molecule in a uniform solvent and the effect of the environment polarity on the charge redistribution. The charge redistribution was obtained from quantum chemical calculations of the dye in a dielectric with the permittivity D, which was in this case different for all points and equal to the static dielectric constant of a solvent $D = \epsilon_{st}$. The optical and static dielectric constants used in calculating E_{sc} for the given charge redistribution were the same as the constants of solvents studied experimentally. For the explanation of the dashed line, see the text. Numbering of the points is the same as in Figure 2.

5 by

$$\frac{\partial}{\partial E_{sc}}\,{}^1/_2(h\nu_a - h\nu_f) = p\left(1 + \frac{M_{3a}kT}{2M_{2a}^2} + \frac{|M_{3f}|kT}{2M_{2f}^2}\right) \qquad (11)$$

which was obtained taking the derivative of the Stokes shift (eq 9) with respect to E_{sc} with the condition of eq 10. Here we have employed approximate equalities $M_2 \approx M_{2is} + 2kTE_s$ and $M_3 \approx M_{3is}$.

The momenta M_2 and M_3 were evaluated from the least-squares fitting of eq 8 to the experimental band shape functions (the results of fitting for acetonitrile solution are shown by solid curves at Figure 1). The values of α were about 0.2; hence, the condition for it (eq 8) is approximately fulfilled. The ratios in the right side of eq 11 turned out to be virtually the same for each group of solvent. Thus, we get for the scaling parameters $p = 4.1 \pm 0.4$ and $p = 3.0 \pm 0.3$ for aprotic solvents and alcohols, respectively. Now, the true E_s can be easily obtained from eq 10 and p.

In order to compare the two solvent groups, we performed the estimates of various parameters for the dye solutions in acetonitrile and in methanol (points 1 and 15 in Figure 5), because these two solvents have similar dielectric constants and practically coinciding values of E_{sc}. The values of the true E_s are found as (1380 ± 140) and (1005 ± 100) cm^{-1}, for acetonitrile and methanol, respectively. The correction to eq 2 due to the term in the square brackets of eq 9 was (650 ± 100) and (720 ± 100) cm^{-1}; the estimates of the inner sphere reorganization energy E_{is} obtained from the experimental Stokes shift and eq 9 were (455 ± 200) and (715 ± 200) cm^{-1}, for acetonitrile and methanol, respectively. The accuracy of the latter estimates does not allow one to conclude if the inner sphere reorganization energies are really different for the two sets of solvents. In any case, they are both definitely positive in concordance with the physical meaning of the inner sphere reorganization energy.

The Value of Scaling Factor. The scaling factor p (of the order of 3−4) standing for the ratio of the true E_s and its calculated value E_{sc} may seem high. In the present study we did not pretend to give precise calculations of the reorganization energy. Our purpose was to obtain some integral characteristic of the surroundings dielectric properties that governs the solvent reorganization energy of the proflavine−solvent system. One should not expect that quantum chemical calculations can give quantitatively perfect results for the solute charge (re)distribution. In the dielectric continuum formalism, the position of the dye surface that forms the cavity is rather arbitrary. All these factors can result in the discrepancy between the data and calculations of 3−4 times.

To test how sensitive the final results of our analysis are to particular form and value of the charge redistribution, we performed the same analysis but using quantum chemical calculations in another, AM1,[34] scheme (and using, less rigorously for this dye, the lowest unoccupied MO of the ground state as the final TMO, see section 6 and ref 20). We obtained different charge redistributions and two times higher values of p. Fortunately, the final results, *viz*., the true values of E_s (cf. E_s of 1280 and 1030 cm^{-1} for acetonitrile and methanol) and E_{is}, turned out to be weakly sensitive to particular charge redistribution.

Deviations from Linear Dependence. Equations 2 and 3 predict a linear dependence between Stokes shift and the solvent reorganization energy. Having extrapolated this dependence to zero value of E_s, one obtains that a half of Stokes shift equals E_{is} at $E_s = 0$. From extrapolation of the straight lines in Figure 5 to $E_{sc} = E_s/p = 0$ we obtain for the intercept *negative* values of (−780 ± 100) and (−460 ± 110) cm^{-1} for aprotic solvents and alcohols, respectively. The inner sphere reorganization energy is of necessity *positive* value. The effective negative values of E_{is} show that the expression for Stokes shift given by eq 2 fails. This contradiction is eliminated in terms of more rigorous eq 9, on which basis physically reasonable estimates of E_{is} have been obtained.

According to eq 9, the dependence of the Stokes shift on the solvent reorganization energy is nonlinear. Extrapolation of the tangential line at a given E_s of the curve determined by eq 9 to the zero E_s gives the intercept

$$E_{is} - \frac{M_{3a}}{4M_{2a}}\left(1 + \frac{2kTE_s}{M_{2a}}\right) - \frac{|M_{3f}|}{4M_{2f}}\left(1 + \frac{2kTE_s}{M_{2f}}\right)$$

which may assume negative values. This explains the data given above. The slope of the dependence of Stokes shift on the solvent reorganization energy predicted from eq 9 is greater than that from eq 2 by factor of about 1.3−1.4. The present example shows that more precise approximation of Stokes shift given by eq 9 results in a value of Stokes shift about 1.6 times lower than the value given in eq 2.

The dashed curve in Figure 5 represents a nonlinear dependence of Stokes shift on the solvent reorganization energy in polar aprotic solvents. This curve was calculated from eq 9 on the basis of the estimates of the momenta given above. One can see that, in the interval studied, the deviation from linear dependence is small. Due to scattering of experimental points in Figure 5, one can not discriminate reliably the linear (solid line) and nonlinear (dashed curve) dependences.

Specific Solvent Effects on Stokes Shift. It is well-known that spectral properties of solutes are influenced specifically by some solvents, and so are those of the dye under study. One can see from Figure 5 that calculations in the framework of the continuum approach cannot explain, first, the gap between the lines for polar aprotic solvents and for alcohols and, second, the different slopes of the two lines.

Quantum chemical calculations of the dye with H-bond (as a donor of H-bond H_2O or CH_3OH molecules were used) have revealed that the effect of H-bonding on charge redistributions is small (the resultant effect on E_{sc} is less than 5%). On the other hand, it is known that H-bonding can result in an additional inner sphere reorganization energy.[35] This effect could be responsible for higher values of E_{is} in alcohols than in aprotic solvents, if any. The solvent reorganization energy in aprotic solvents is greater by about 15%−30% than that in alcohols (cf. E_s for acetonitrile and methanol). According to eq 9, these effects can explain formally the different slopes of and the gap between the lines in Figure 5 for the two sets of solvents. Perhaps, the lower values of E_s in alcohols are due to distortion of H-bonds between alcohol molecules adjacent to the solute.

The anomalous solvent for PF is water. The observed Stokes shift in water is 1500 cm^{-1} (not shown), which is much higher than its estimates based on the parameters extracted from the data for aprotic solvents (1100 cm^{-1}) and alcohols (990 cm^{-1}). Perhaps, such behavior of water solvent is due to a three-dimensional H-bond network of water molecules in which the dye is incorporated. Another example of specific solvent effect is benzonitrile (its $\epsilon_{st} = 25.5$) in which Stokes shift is also too high (see point 19 in Figure 2). In this solvent the fluorescence quantum yield is abnormally higher (about two times) than in the other solvents. We suppose that donor−acceptor complex with PF typical of aromatic solvents is formed here. We also found that another aromatic solvent, nitrobenzene, forms a specific complex with PF that results in a complete quenching of the dye fluorescence.

Specific Effects of Solvent Mixtures on Stokes Shift. It is well-known that for a mixture of two solvents, for which the nature of the specific effect of each pure solvent on spectral properties of the chromophore is different (*e.g.*, different type of H-bonding), abnormal behavior of Stokes shift is observed (see, *e.g.*, ref 27). We studied the mixtures of polar aprotic solvents each of them, as discussed above, having no specific effects, and observed another kind of effect on the solvent reorganization energy.

In such mixtures, one of the components of the mixture solvates preferentially the solute. The reason for preferential solvation can be the difference in affinity to cation (different solvent donor numbers, DN[36]) or a large difference of the permanent dipolar momenta of the solvent molecules of the two components of the mixture. The examples are acetonitrile (DN = 14, $\epsilon_{st} = 37$)−*N*,*N*-dimethylformamide (DN = 27, $\epsilon_{st} = 37$) mixture (point 20 in Figure 2), 1,4-dioxane ($\epsilon_{st} = 2.2$)−γ-butyrolactone ($\epsilon_{st} = 42$) (point 21), acetonitrile−dichloroethane ($\epsilon_{st} = 10$, DN = 0.1) (point 22), and acetone ($\epsilon_{st} = 21$, DN = 17)−dichloroethane (point 23) mixtures. In all these mixtures Stokes shift is abnormally high. To the contrary, mixtures of solvents having similar polarity and affinity to cations (*e.g.*, points 2, 4, 5, 7 in Figure 2) behave like individual solvents.

The qualitative explanation of the specific effect of mixtures on the solvent reorganization energy is the following. The local concentration of the component of a mixed solvent having, say, higher affinity to cation (or higher permanent dipole) is greater at a site of the solute bearing positive charge. The instantaneous transfer of this positive charge to another neutral solute site costs an additional increase of the new state's energy because the local concentration of the higher affinity species here is lower than that near the initial site. This energy increase brings about additional contribution to the solvent reorganization energy as compared to any of the two pure solvents which have similar concentration at the two sites. It is this "concentrational" reorganization free energy that results in abnormally high values of Stokes shift in the above mentioned specific mixtures of "nonspecific" solvents. This effect of preferential solvation on E_s was observed and explained earlier.[37,38]

The individual solvent dichloroethane provides a mixture of *trans*- and *gauche*-isomers, the former possessing zero dipolar moment.[39] Therefore, the solvation by this solvent should be somewhat stronger than by the media of the same static permittivity due to an enhanced local concentration of polar *gauche*-isomer around the charged groups. This fact and the effect of "concentrational" reorganization can explain somewhat enhanced Stokes shift for this solvent (point 7, Figure 5).

Absorption and Fluorescence Maxima and the Static Dielectric Properties of the Environment. As it was discussed in the Introduction, static dielectric properties of the solvent may be studied with the help of the sum of the energy of absorption and emission maxima (see eqs 2 and 6). However, we found that there is no correlation between the sum of the absorption and emission maxima of PF (for pure solvents and mixtures that behave like individual solvents) and ϵ_{st} and that the correlation between the free energy gap and the static dielectric properties of the environment is not observed. This means that the total change of the equilibrium free energy upon optical transition of the system under study is influenced substantially by nonelectrostatic interactions. No explanation was found for the fact that there is a slight tendency for the equilibrium free energy gap to decrease upon increasing the optical dielectric constant of the solvent (plot not shown).

4. Experimental Section

Materials. Proflavine (3,6-diaminoacridine) hydrochloride was purchased from Sigma. Phosphorus triiodide, benzonitrile (HPLC grade), and dichloromethane (HPLC grade) were purchased from Aldrich. The other reagents (all of special purity grade "OSCH") were purchased from Reakhim.

Instruments. Absorption spectra were recorded on Specord M40 spectrophotometer using a 10 mm path length quartz cell. This device records spectra at a slit width fixed in terms of frequency units. The slit width was 40 cm^{-1}. The scanning speed was 100 cm^{-1}/min. The time constant was 1 s. Optical density of the dye solutions at the absorption maximum was from 0.1 to 0.5 per cm (dye concentration $(2-10) \times 10^{-6}$). The band maximum was determined with the aid of instrumental function. The spectrum was recorded several times so that the accuracy of the measurement of absorption band maximum would be 4 cm^{-1}.

It was essential for the present study to record true (corrected, *i.e.*, normalized to the spectral function of the emission monochromator−detector system of the fluorometer) fluorescence spectra. If all spectra studied had the same bandwidth and close values of maxima, the correction would result in a shift of the value of emission maximum identical for all spectra, and the correction procedure could be omitted. However, the tendency for the bandwidth to decrease with decrease of the solvent reorganization energy was observed, and therefore, uncorrected spectra would give rise to improper slopes of the dependences studied.

Corrected fluorescence spectra were recorded on a Hitachi 850 fluorometer at a slit width of emission of 2 nm using a 10 mm quartz cell. The scanning speed was 5 nm/min. The time response was 2 s. The dye was excited at the absorption band maximum. Advantage was taken of using the standard procedure of spectrum correction including a rhodamin B quantum counter and a light diffuser. Such a correction provides an emission spectrum in terms of the amount of quanta per unit wavelength interval. We performed additional manual calibration of the excitation and emission monochromators using a narrow line of 435.8 nm of a low-pressure Hg-lamp. This procedure increased the wavelength accuracy of the device up to 0.1 nm. Optical density of the dye solutions in the absorption maximum was less than 0.15 (dye concentration less than 3×10^{-6} M). The emission band maximum was determined as a wavelength that gives zero to the value of the first derivative of the spectrum with respect to wavelength. The first derivative was calculated using instrumental function. The spectrum was recorded several times so that the accuracy of the measurement of emission maximum would be 0.1 nm. This value is two times better than the standard accuracy of the fluorometer utilized.

Corrected (normalized to the spectral function of the light source-excitation monochromator system) spectra of fluorescence excitation were recorded on the same fluorometer at a slit width of excitation of 5 nm, a scanning speed of 12 nm/min, and a time response of 2 s using a 10 mm quartz cell (dye concentration less than 2×10^{-6} M). The procedure for measurement of the excitation maximum was the same as that of the emission maximum.

To obtain the band shape function from the absorption and emission spectra recorded as described above, one should divide the intensity of the spectra by the frequency to the first and fifth (to the third due to the Einstein coefficient for spontaneous emission and to the second due to drawing the slit width from wavlength to frequency units) power, respectively.[10] In our experiment, such procedure resulted in increasing the value of the Stokes shifts by a value (of about 280 cm^{-1}) virtually the same for all liquids. Additional practically constant differences between the true maxima of the spectra and the measured ones were due to instrumental functions for getting the specta's maxima (see above). The overall correction to the half—Stokes shift was 170 cm^{-1}. The true Stokes shift was obtained from the measured one by adding this correction.

The spectrum of fluorescence polarization was recorded on the same fluorometer using the standard single-beam method (see, *e.g.*, ref 27) at the excitation monochromator slit of 2 nm. The wavelength of emission monochromator with a 5 nm slit was fixed at 495 nm (close to the emission maximum of the dye). Dye concentration was 3×10^{-6} M.

Solutions. The solutions with the dye concentration in the range $(1-10) \times 10^{-6}$ M were used. All measurements were performed at 18−21 °C. In dimethyl sulfoxide, dimethylformamide, butanol, and their mixtures a deprotonation of the dye was observed. To avoid deprotonation, 100% H_2SO_4 was added to the solutions to the concentration of 10^{-4} M.

Dicationic dye is capable of forming ion pairs with its counterion. The independence of the spectral characteristics from the concentration of the dye and of the emission spectrum from the excitation wavelength indicated that there was no ion pairing in all but two solutions. In low dielectric permittivity (of 9 and 10.5) solvents dichloromethane and dichloroethane, a marked fraction (of the order of 50% and 15%) of the dye molecules exists in ion pairs with Cl^- or other, if any, anions, which was estimated from the observed distortion of the solutions spectra. Absorption and emission spectra of the ion pairs overlap with corresponding spectra of the free PF and prevent the quantitative measurements of the free dye's spectral properties. To study the properties of the free dye the following method was employed.

It was found that the dye fluorescence is quenched by iodide anion, quenching in water obeying the Stern−Volmer law. This suggests the dynamic kind of quenching. The constant of dynamic quenching turned out to be higher than the expected value of the bimolecular collision rate constant for neutral reagents of the chromophore and the quencher sizes. This means that at every collision of the excited dye with iodide anion the excited dye undergoes radiationless transition (see, *e.g.*, ref 27). The idea of our method is to make PF form ion pairs predominantly with I^- as the counterion, which was achieved when the I^- concentration was much greater than the overall concentration of the other anions in the solution. The fluorescence of the dye in complex with the quenching counterion proved to be completely suppressed, and only free dye molecules contribute to the emission spectrum. As to the absorption spectrum, ion pairs still interfere with the observation of the free dye. Instead of the absorption spectrum, the excitation spectrum of the dye fluorescence was studied. Only free dye molecules contribute to the excitation spectrum, since the intensity of the excitation spectrum is proportional to the number of emitted quanta at a fixed emission wavelength, which, in turn, is proportional to the number of quanta absorbed by the emitting species. The latter is not affected by absorbing ion pairs because: (i) the intensity of the excitation beam was practically constant along its path due to low optical density (less than 0.1) of the solution used; (ii) the radiationless energy transfer from the excited ion pairs to the free species should be negligible due to very short lifetime of the excited state of the ion pairs (practically zero fluorescence quantum yield) and low concentration of the solution.

It was found that in other aprotic solvents (points 1−11 in Figure 2) and in alcohols (points 14−18) the maxima of absorption and excitation spectra differ by the same constant value of about 1 nm due to difference in recording methods of the spectrophotometer and fluorometer employed. This correction was used to find the absorption maximum from the excitation spectrum in dichloromethane and dichloroethane solutions.

Iodide anion was added in solution (without H_2SO_4) as an excess of HI. The gaseous HI was formed upon contact of phosphorus triiodide with water vapor in nitrogen atmosphere. Pure solvent without the dye was maintained in HI-containing atmosphere for 0.5−1 h. Solution containing HI was added stepwise to the dye solution until the shape and maxima of the excitation and emission spectra (but not the intensity) stopped changing upon addition of HI solution. (This means that the dye existed in free form and in ion pairs formed predominantly with iodide anions.) It was found that for the resulting solution the position of emission maximum is independent of the excitation wavelength, and *vice versa*, the position of excitation maximum is independent of the wavelength at which the emission was monitored. This means that spectral properties of only free dye are observed and that the fluorescence of all ion pairs is completely quenched.

For dichloroethane solutions, these data (with HI) were compared with the data (with H_2SO_4) obtained by an independent method. The absorption and emission spectra of the ion pairs are shifted to the high and low-frequency sides, correspondingly, with respect to the corresponding spectra of the free dye. To register the properties of the free dye, the wavelength of the excitation beam was shifted from the absorption maximum to the red side until the emission maximum stopped changing when the wavelength of excitation was shifted. Similarly, the wavelength at which the emission was monitored was shifted from the fluorescence maximum to the blue side until the excitation maximum changed. Both methods (with H_2SO_4 and HI) gave the same results.

5. Calculations of the Solvent Reorganization Energy

For calculation of the solvent reorganization energy E_{sc}, we employed the concept of transition molecular orbitals.[20] This model allows one to employ "fixed charge density" formulation[24,25] for calculation of the reorganization energy provided the explicit charge redistribution of the solute is derived from transition molecular orbitals (TMO).[20] The solute embedded in the solvent is described as a cavity in a continuum dielectric. The charge redistribution $\Delta\rho$ was calculated as the difference of the electronic densities of the two TMOs

$$\Delta\rho = \rho(\text{HSMO}) + \rho(\text{LSMO}) - 2\rho(\text{HOMO}) \qquad (12)$$

namely, the highest and the lowest singly occupied MOs (HSMO and LSMO) of the excited state and the highest occupied MO (HOMO) of the ground state, the factor 2 being due to double occupancy of HOMO. Redistribution of the other MOs is described as polarization of the effective electronic continuum.[20] Quantum chemical calculations of proflavine in dicationic form were performed in the PM3 semiempirical scheme.[40] The ground and excited states were calculated in their equilibrium reaction fields produced by the environment polarization. The account of equilibrium solvent effects was taken using modification[41,42] of the self-consistent reaction field theory[43] based on continuum approximation. This modification was implemented in the MOPAC package (version 6.0).[44] The protocol[41,42] makes possible semiempirical calculations of the wave functions of solute in the self-consistent reaction field of surrounding continuum dielectric with permittivity D. For all calculations the geometry of the molecule in the ground state in gaseous phase was chosen.

In terms of the fixed charge density formulation, the expression for the solvent reorganization energy is[24,25]

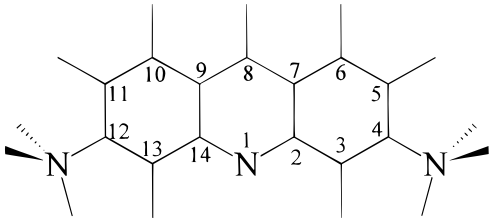
$$E_s = {}^1\!/_2\int_V d\mathbf{r}\;\varphi_{op}(\rho_{eff}(\mathbf{r}))\;\rho_{eff}(\mathbf{r}) - {}^1\!/_2\int_V d\mathbf{r}\;\varphi_{st}(\rho_{eff}(\mathbf{r}))\;\rho_{eff}(\mathbf{r}) \qquad (13)$$

$$\rho_{eff}(\mathbf{r}) \equiv \Delta\rho(\mathbf{r})$$

where $\Delta\rho(\mathbf{r})$ is the charge redistribution function and φ is the electrostatic potential that is derivable from the solution of the electrostatic problem for the effective charge distribution $\Delta\rho(\mathbf{r})$. The subscript *st* refers all terms of this equation to the case when the electrostatic problem is solved for the dielectric constant (generally a function of coordinates) equal to the static dielectric constant of the system, $\epsilon_{st}(\mathbf{r})$. The subscript *op* refers to the case when the optical (high-frequency) dielectric constant of the same system, $\epsilon_{op}(\mathbf{r})$, is used.

To calculate the reorganization energy from 13 the solution of two electrostatic problems was found: first, φ_{st} for the real medium with the static dielectric constant of the external continuum, ϵ_{st}, and the static dielectric constant of the solute cavity that coincides with the optical one, ϵ_{in}, and second, φ_{op} for the effective medium with the optical dielectric constant of the external continuum, ϵ_{op}, and the optical dielectric constant of the cavity, ϵ_{in}. The effective charge distribution $\Delta\rho(\mathbf{r})$ used for both problems *must be the same* (fixed charge density formulation).[20,24,25] Note that the charging energies in the two media (eq 13) are only auxiliary quantities serving for the calculations of E_s for a given charge redistribution.

SCHEME 1: Dicationic Dye Proflavine[a]



[a] Numerbing of the dye atoms is shown.

The Charge Redistribution Function. Quantum chemical calculations showed that, for the $\pi-\pi$ transition between the ground and the lowest excited states of the dye, the contributions to TMOs are made predominantly by 2p-AOs that are perpendicular to the plane of the molecule (Scheme 1). There are small contributions to the TMOs of NH_3^+ groups, namely, of 2p-AOs of nitrogen-atom and 1s-AOs of hydrogen atoms that are out of the plane of the molecule. The contribution of these AOs to the charge redistribution function are more than 20 times lower than that of 2p-AOs of atoms constituting conjugated rings. In order to simplify calculations, charge redistribution due to NH_3^+ was artificially removed from these groups and added to charge redistribution due to C4 and C12 atoms. We estimated that the effect of such simplification on the value of the solvent reorganization energy was less than 3%.

The electronic density of TMOs was represented by a sum of the densities of separate AOs; that is, we neglected the contributions from overlapping AO wave functions since in semiempirical quantum chemical calculations wave functions are normalized neglecting the overlapping of AOs (NDDO approximation). We estimated that the appropriate allowance for such terms[20] would affect the absolute value of E_{sc} by less than 7%, having no effect on relative dependences of E_{sc} on any parameter of the model. As it was described previously,[20] electronic density of each 2p-AO was approximated by a pair of spherical charges of 0.5e having uniform density within the cutoff sphere (of 0.7 Å, *i.e.*, about a half of C−C bond length) and zero outside the sphere. The distance between the centers of the two spheres was 1.8 Å. The resultant charge redistribution function $\Delta\rho(\mathbf{r})$ was also approximated as a set of the pairs of spherical charges.

The Cavity. The surface of the flat molecule of proflavine was approximated by an oblate spheroic cavity with semiaxes $A = 5$ Å and $B = 1.8$ Å. The center of oblate spheroid was placed at the center of the segment connecting N1 and C8 atoms. The plane of gyration of oblate spheroid coincides with the plane of aromatic rings of the dye. The x and y coordinates of the calculated effective charges were taken at positions of appropriate atoms corresponding to optimized dye geometry in gas phase. The z coordinates of the centers of the two spheres approximating $2p_z$ orbitals should have been ±0.9 Å. However, due to an imperfect approximation of proflavine cavity by the oblate spheroid, the location of charge centers would be too close to the cavity surface. Therefore, we decided to set z coordinates of the charge centers to be proportional to the distance between XOY plane and the point on the spheroid surface with the same x and y coordinates: $z = \pm 0.9\,(1 - (x^2 + y^2)/A^2)^{1/2}$ (Å). Thus, z coordinates of the dye charges were in the range $0.6\text{ Å} < |z| < 0.9\text{ Å}$. The dielectric constants of effective electronic continuum inside the cavity was $\epsilon_{in} = 2.4$, which is close to the optical constant of most aromatics.[20]

The solution of the electrostatic problem for a set of spherical charges inside the cavity coincides with that for the corresponding set of point charges.[20] The analytical solution of the electrostatic problem for a set of point charges inside oblate spheroid cavity was taken from ref 45. In evaluating the integrals in eq 13, we used point charge approximation of spherical charges: the integrals were replaced by the products of the potentials at the center of each spherical charge and its total value. This approximation results in the error in the value of the reorganization energy not greater than 5%.[20]

6. Conclusions

In the present work, we tried to answer the question whether the Stokes shift can serve as a probe of the solvent reorganization free energy and got the affirmative answer. For a stokes shift to serve as a tool for probing the solvent reorganization free energy, first of all, the system chromophore−solvent should comply with a set of definite conditions. If the conditions are met, it is possible to extract the solvent reorganization energy from the data on the Stokes shift in a set of solvents. Then, additional features of spectral bands such as spectrum momenta should be studied.

An important point required for spectroscopic studies of the solvent reorganization energy is the relation between the solvent reorganization energy and the dielectric properties of the solvent. This relation can be correctly described provided two effects are taken into account. First is the dielectric inhomogeneity caused by incorporation of a bulky solute molecule in a uniform solvent; this effect was calculated with the aid of the dielectric cavity model. The second effect is the influence of the solvent polarity on the charge redistribution upon the electronic transition that gives rise to reorganization of the polar surroundings, this influence was calculated quantum chemically in the framework of the continuum self-consistent reaction field theory.

Theoretical estimates of the solvent reorganization energy presented here are based on continuum description of the solvent. The correlation between experimental data and the estimates shows that continuum approach is able, at least in the present case, to describe correctly the relation between the solvent reorganization energy and the dielectric properties of the solvent. However, the observed experimentally 15%−30% difference in the values of solvent reorganization energy for polar aprotic solvents and for alcohols cannot be explained in terms of continuum approach.

A commonly adopted equation for Stokes shift establishes the equality between Stokes shift and the doubled reorganization energy (eq 2). According to this equation, the intercept of the dependence of Stokes shift on the solvent reorganization energy gives the doubled inner sphere reorganization energy. We found that the value of the intercept is negative for our experimental system. This result implies that eq 2 is generally not rigorous, and it is consistent with a more precise approximation of Stokes shift (eq 9), which takes into account quantum nature of the solute local modes. The latter results in the nonlinear dependences of both the Stokes shift and the maxima of absorption and emission bands on the solvent reorganization energy. The inner sphere reorganization energies calculated on account of this effect are essentially positive.

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