Journal of Photochemistry, *30* (1985) 13 - 23

THE INFLUENCE OF A POLAR MEDIUM ON THE RATE OF FAST PHOTOPROCESSES

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(Received April 24, 1984; in revised form July 27, 1984)

Summary

Many photoprocesses include a radiationless non-adiabatic transition $\Psi_2 \rightsquigarrow \Psi_1$ at a critical geometry where the gap between the energy surfaces is small. Owing to the significant redistribution of the molecular charge the polar medium has a strong influence not only on the potential energy but also on the reaction coordinate. A statistical method which allows the solvent reorganization effect to be described has been suggested for the case when the potentials of both the initial and final states in the polar medium have local minima at some critical geometry. Its application to the photoisomerization of cyanine dyes is discussed.

1. Introduction

Many photoprocesses, such as singlet–singlet and triplet–triplet energy transfer, isomerization reactions etc., have a common feature. In contrast with thermally activated reactions these processes occur in two steps (Fig. 1): after excitation of the species an energy barrier $\tilde{U}_0$ on the excited state surface is overcome and then a radiationless transition $\Psi_2 \rightsquigarrow \Psi_1$ takes place at a critical geometry where the energy gap between $\tilde{U}_1$ and $\tilde{U}_2$ is small enough (about 1 - 2 eV) for the probability of such a transition to be significant. In Fig. 1 the path of such a process is shown by arrows: q' is the reaction coordinate in the gas phase (or in a non-polar medium), $q' = q'_0$ corresponds to the critical geometry, and regions a and c correspond to the reactants and products respectively.

It has been shown by Velsko and Fleming [1] and Rentsch [2] that in the case of the isomerization of polymethine dyes in polar solvents the rate of population of the local minimum of the excited state potential at $q' = q'_0$ is sufficiently large at room temperature for the preferred path for the deactivation of the photoexcited state to be that shown by arrows

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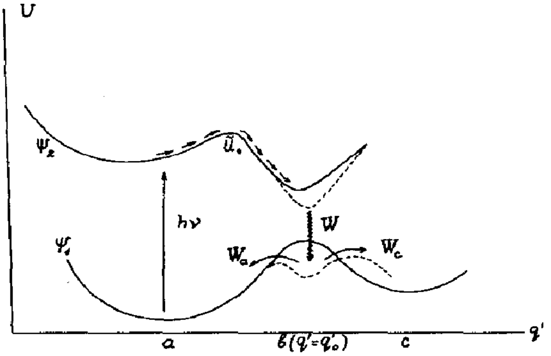

Fig. 1. Curves of the potential energy $\tilde{U}_1$ and $\tilde{U}_2$ for the isomerization reaction as a function of the intramolecular coordinate q': ——, gas phase; - - -, polar solvent. Regions a and c correspond to the reactants and products respectively, and region b corresponds to the critical geometry $q' = q'_0$.

in Fig. 1. Therefore, the probability that a radiationless transition will take place is significant. Such a transition can affect other deactivation channels, *e.g.* the fluorescence decay kinetics [3, 4].

Two aspects of the effect of the medium on the rate constants of the photoprocesses are discussed in the literature. Firstly the effect of the viscous drag on the motion along the reaction coordinate has been investigated [5 - 7] and has been found to lead to a change in the energy barrier $\tilde{U}_0$ (Fig. 1). Secondly the effect of polar solvents on the potential energy surfaces has been studied [8, 9]. The difference between the potential energy surfaces in a polar medium and in the gas phase (or in a non-polar solvent) is particularly large for photoisomerization reactions which proceed via a torsional motion around a C—C bond because this motion is accompanied by charge transfer [8, 10]. In the case of polar solutions the potential energy surfaces in the ground and first excited states may have local minima at the critical geometry, whereas in the gas phase (or in a non-polar medium) the ground state surface has a maximum at this geometry (Fig. 1).

In both cases the problem of determining the effects of the medium reduces to the correct evaluation of the potential energy surfaces in the polar solvent. Despite the importance of this aspect, such an approach takes into account only the static effects on the potential energy surfaces and does not include analysis of the liquid dynamics. Therefore it seems to be unsatisfactory. In the present paper we use the quantum-classical approximation [11] in an attempt to develop a consistent description of the effects of polar media on the probability of radiationless transition.

As has been mentioned earlier the population of the local minimum of $\tilde{U}_2$ at $q' = q'_0$ proceeds at a faster rate than any of the other processes of deactivation of the photoexcited state. We assume that in a polar solvent a quasi-equilibrium distribution of the nuclear system in this minimum is established and that this should be treated as the initial condition of the kinetic stage [12]. This assumption is valid if the probability per unit time of the radiationless transition is much less than the rates of vibrational and polarization relaxation of the nuclear system [2]. Thus it is necessary to determine the decay with time of the quasi-equilibrium distribution due to the non-adiabatic interaction.

2. Method

Only two adiabatic electronic states Ψ_1 and Ψ_2 with adiabatic potentials $\tilde{U}_1(q)$ and $\tilde{U}_2(q)$ respectively need be taken into account in the region where the potential surfaces approach each other (Fig. 1, region b). If the nuclear subsystem is classical it can be described by the 2 X 2 density matrix $\hat{\tilde{\rho}}$ [11]. The diagonal elements $\tilde{\rho}_{ii}(p, q, t) \equiv \tilde{\rho}_i(p, q, t)$ represent the classical distributions of the nuclear coordinates q and impulses p in the electronic states Ψ_i, and the non-diagonal elements $\tilde{\rho}_{ik}(p, q, t)$ represent the phase relations between the quantum states Ψ_i and Ψ_k ($i \neq k$, $i, k = 1, 2$). The set (p, q) consists of the nuclear coordinates and impulses $(p_{\text{int}}, q_{\text{int}})$ and (p_s, q_s) of the reactants and solvents respectively. In the following treatment we assume that the internal coordinate set $(p_{\text{int}}, q_{\text{int}})$ consists of a single degree of freedom (p', q') which is the reaction coordinate in the gas phase.

The equation for the density matrix is of the Liouville type [11] and describes the time evolution of the system with the hamiltonian

$$\hat{H} = K + \tilde{\bar{U}} + \Delta\tilde{U}\hat{\sigma}_3 + V\hat{\sigma}_2 \tag{1}$$

where the $\hat{\sigma}_i$ $(i = 1, 2, 3)$ are Pauli matrices, K is the kinetic energy of the nuclei, $\tilde{\bar{U}} = (\tilde{U}_2 + \tilde{U}_1)/2$, $\Delta\tilde{U} = (\tilde{U}_2 - \tilde{U}_1)/2$ and V represents the non-adiabatic interactions proportional to the velocities of the atomic nuclei [11].

In this paper we assume that the potential surfaces in both the initial and final states have local minima at a critical geometry in a polar medium (Fig. 1). Then the process under discussion, which can be described as movement of the representative point from region b of the excited state potential $\tilde{U}_2$ to region c of the ground state potential $\tilde{U}_1$, consists of two steps: a radiationless transition $\Psi_2 \rightsquigarrow \Psi_1$ in region b and a thermally activated transition in the state Ψ_1 to the product region c. We assume that region b which is a region of quasi-equilibrium can be treated as a relatively long-lived transient (isomer) with a characteristic electronic and vibronic spectrum [13, 14]. The adiabatic potentials $\tilde{U}_1$ and $\tilde{U}_2$ can then be approximated as the sum of two independent contributions [15]:

$$\begin{aligned} \tilde{U}_1 &= U_1'(q') + \tilde{U}_1''(q_s) \\ \tilde{U}_2 &= U_2'(q') + \tilde{U}_2''(q_s) \end{aligned} \tag{2}$$

where $U_1'(q')$ and $U_2'(q')$ depend only on the intramolecular coordinate q' and correspond to the potentials in the gas phase, and $\tilde{U}_1''(q_s)$ and $\tilde{U}_2''(q_s)$ involve the interaction between the polar medium and the transient in which the internal coordinates are fixed and are equal to their equilibrium values in region b.

The Liouville operators $\tilde{L}_1$ and $\tilde{L}_2$, which describe the dynamics of the system in the electronic states Ψ_1 and Ψ_2 respectively, can be represented, by analogy with eqn. (2), as the sums [15]

$$\begin{aligned} \tilde{L}_1 &= L'_1 + \tilde{L}''_1 \\ \tilde{L}_2 &= L'_2 + \tilde{L}''_2 \end{aligned} \tag{3}$$

where the dynamic operators $L'_{1,2}$ denote the one-dimensional Poisson brackets

$$L'_{1,2}\ldots = \frac{\partial U'_{1,2}}{\partial q'}\frac{\partial\ldots}{\partial p'} - \frac{p'}{m'}\frac{\partial\ldots}{\partial q'} \tag{4}$$

The expressions for the operators $\tilde{L}''_{1,2}$ are analogous but they consist of a very large number of terms.

The contribution of the solvent atomic nuclei to the non-adiabatic interaction in the case of fast relaxation of their velocities can be neglected. Thus the non-adiabatic interaction consists of a single term proportional to the velocity of the intramolecular motion [11]:

$$V = \frac{\hbar p'\Delta F\Gamma_0}{2m'(\Delta U' + \Delta\tilde{U}'')^2} \tag{5}$$

where ΔF is the difference between the diabatic potential ranges in the gas phase in the region $q' = q'_0$ at which they cross, $2\Gamma_0$ is the energy gap in the gas phase, $\Delta U' = (U'_2 - U'_1)/2$ and $\Delta\tilde{U}'' = (\tilde{U}''_2 - \tilde{U}''_1)/2$.

It can be concluded from eqns. (2), (3) and (5) that the many-particle effects in the Liouville equation enter only through the Poisson brackets $\tilde{L}''_{1,2}$ and the difference

$$Q = \Delta\tilde{U}'' = \frac{\tilde{U}''_2 - \tilde{U}''_1}{2} \tag{6}$$

This means [15] that the time evolution of the system can be described by the partial density matrix $\hat{\rho}(p', q', Q, t)$ which depends on a single solvent collective coordinate Q.

As the potentials $\tilde{U}_1$ and $\tilde{U}_2$ in polar solvents have minima at $q' = q'_0$, the time evolution of Q has the characteristics of a relaxation process in both the initial and final states. $Q(t)$ is usually considered [16, 17] to be a quasi-stationary fluctuation [18] in polar media. Then the effective operators $L''_1(Q)$ and $L''_2(Q)$, which describe the time evolution of the Q coordinate of the medium in the electronic states Ψ_1 and Ψ_2, can be expressed as diffusion operators in the effective potentials U''_1 and U''_2 [15 - 17]:

$$L''_{1,2}\ldots = D\left\{\frac{\partial^2\ldots}{\partial\chi^2} + \frac{1}{T}\frac{\partial}{\partial\chi}\left(\ldots\frac{\partial}{\partial\chi}U''_{1,2}\right)\right\} \tag{7}$$

where

$$\chi = \frac{2Q - \Delta''}{(2E_r)^{1/2}}$$

$$D = \frac{T}{\tau_s}$$

$$U_1'' = \frac{\{\chi - (E_r/2)^{1/2}\}^2 - \Delta''}{2}$$

$$U_2'' = \frac{\{\chi + (E_r/2)^{1/2}\}^2 + \Delta''}{2}$$

E_r is the energy for reorganization in the medium owing to the electronic transition $\Psi_2 \rightsquigarrow \Psi_1$ at $q' = q_0'$, Δ'' is the difference between the equilibrium polarization energies in the states Ψ_2 and Ψ_1 at this geometry, τ_s is the relaxation time of the orientation polarization of the solvent and T is the temperature in units of energy.

The equation for the partial density matrix $\hat{\rho}(p', q', Q, t)$ is [15]

$$\frac{\partial \hat{\rho}}{\partial t} = \frac{\mathrm{i}}{\hbar}\left[\hat{\rho}, \hat{1}\left\{\Delta U' + \chi\left(\frac{E_r}{2}\right)^{1/2} + \frac{\Delta''}{2}\right\} + V\hat{\sigma}_2\right] + \frac{L_2 + L_1}{2} + \\ + (L_2 - L_1)\frac{\hat{\rho}\hat{\sigma}_3 + \hat{\sigma}_3\hat{\rho}}{4} \qquad (8)$$

$L_{1,2} = L_{1,2}' + L_{1,2}''$ (see eqns. (4) and (7)) and the non-adiabatic interaction V is given by eqn. (5). This equation is solved using the initial conditions

$$\rho_{ik}(p',q',\chi,0) = \delta_{i2}\delta_{k2}\rho_{\mathrm{eq}}'(p',q')\rho_{\mathrm{eq}}''(\chi)$$

$$\rho_{\mathrm{eq}}'(p',q') = \mathrm{const} \times \exp\left\{-\frac{U_2'(q')}{T}\right\} \qquad (9)$$

$$\rho_{\mathrm{eq}}''(\chi) = \mathrm{const} \times \exp\left\{-\frac{U_2''(\chi)}{T}\right\}$$

which correspond to the quasi-equilibrium distribution of the nuclear subsystem in the local minimum of the excited state potential U_2.

The probability of the radiationless transition $\Psi_2 \rightsquigarrow \Psi_1$ in region b is [15]

$$P(t) = \int_{\mathrm{b}} \mathrm{d}p'\,\mathrm{d}q'\,\mathrm{d}\chi\,\rho_1(p',q',\chi,t) \qquad (10)$$

The effective potentials

$$
\begin{aligned}
U_1 &= U_1'(q') + U_1''(\chi) \\
U_2 &= U_2'(q') + U_2''(\chi)
\end{aligned}
\tag{11}
$$

which replace the real potentials (2) in eqn. (8) are paraboloidal in the region $q' = q_0'$ corresponding to the critical geometry (Fig. 2). These potentials intersect at $\chi^* = -\Delta_{eff}/(2E_r)^{1/2}$ where $\Delta_{eff} = 2\Gamma_0 + \Delta''$ is the difference between the minimum energies ($\Delta_{eff} = (U_2)_{min} - (U_1)_{min}$ (Fig. 2)) and $2\Gamma_0$ is the energy gap in the gas phase. The non-adiabatic interaction is greatest in the region (q_0', χ^*); therefore the dominant contribution to the probability (10) comes from this region, and

$$P(t) \approx W(q_0', \chi^*)t$$

where $W(q', \chi^*)$ is the probability per unit time of a radiationless transition. Since the effective potentials given by eqn. (11) intersect along the solvent coordinate χ, the probability $W(q', \chi^*)$ has the usual Arrhenius form

$$W(q', \chi^*) = \omega_{eff} \exp\left(-\frac{U_0}{T}\right) \tag{12}$$

It is not necessary to solve eqn. (8) in order to obtain the main parameter, *i.e.* the activation energy U_0. Under the condition $U_0 \gg T$, U_0 is approximately equal to the height of the crossing point (q', χ^*) above the potential minimum of the initial state (Fig. 2):

$$U_0 = \frac{(E_r - \Delta_{eff})^2}{4E_r} \tag{13}$$

The frequency ω_{eff} at which the region $\chi = \chi^*$ is attained is the average of the intramolecular frequency Ω and the solvent relaxation rate τ_s^{-1}. Its value can be obtained by solving eqn. (8) for the initial conditions (9). However, this problem is not actual because the activation energy U_0 cannot be calculated with sufficient accuracy. It has recently been shown by Zusman [19] that in the special case $\Omega \gg \tau_s^{-1}$

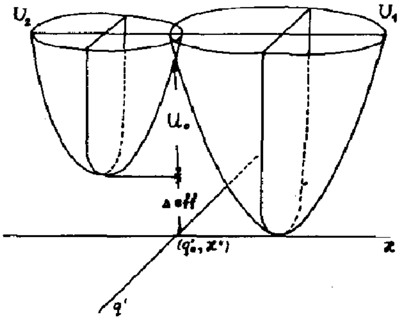

Fig. 2. The paraboloidal effective potentials $U_2(q', \chi)$ and $U_1(q', \chi)$ (eqn. (11)): U_0 is the height of the crossing point (q', χ^*) above the minimum of U_2 and Δ_{eff} is the difference between the values of potential minima.

$$\omega_{\mathrm{eff}} = \frac{\tau_s^{-1}}{\pi} \sin \frac{(E_r + \Delta_{\mathrm{eff}})\pi}{2E_r} \left(\frac{E_r}{\pi T}\right)^{1/2}$$

Equation (12) gives an estimate of the probability per unit time of the radiationless transition at the critical geometry $q' = q'_0$. As a result of this transition the system is in the local minimum of the ground state potential (Fig. 1). The product region c can be reached by an activation transition over the energy barrier (Fig. 1). The probabilities per unit time of the forward and backward reactions (to the product and reactant regions respectively) are

$$\begin{aligned} W_c &= \omega_c \exp\left(-\frac{U_c}{T}\right) \\ W_a &= \omega_a \exp\left(-\frac{U_a}{T}\right) \end{aligned} \qquad (14)$$

ω_a and ω_c are effective frequencies which depend on the solvent viscosity [20], and U_c and U_a are the energy barrier values for the forward and backward pathways along the coordinate q' in the medium.

3. Discussion

The results obtained illustrate the significant effect of a polar medium on the dynamics of the photoprocesses under discussion. This effect leads to a shift of the potential energy surfaces in polar solvents relative to those in the gas phase or in non-polar solvents. It has also been shown that in a polar medium the reaction coordinate coincides with the aggregate coordinate χ of the solvent which describes the reorganization in the medium owing to the electronic transition $\Psi_2 \rightsquigarrow \Psi_1$ at $q' = q'_0$, whereas in the gas phase the coordinate q' of internal motion plays the role of a reaction coordinate. The energy E_r for reorganization of the medium can be large ($E_r \gtrsim$ 1 eV) as a result of the substantial difference between the charge distributions of the transient at configuration $q' = q'_0$ in the electronic states Ψ_2 and Ψ_1. Thus the influence of the polar medium on the rate constant of the radiationless transition can be significant.

We shall now discuss the photoisomerization reaction of the streptocyanine dye pentamethinecyanine in a polar solvent (water) using the method discussed above.

The reaction proceeds by torsion around bonds 3—4 and 2—3 in the molecule (Fig. 3). The corresponding potential energy curves in water [8] are shown in Fig. 4. The potential energy curves in the gas phase were obtained using a Pariser—Parr—Pople calculation including a doubly excited electron configuration, and the solvation energies were evaluated by means of a model corresponding to Klopman's solvation concept.

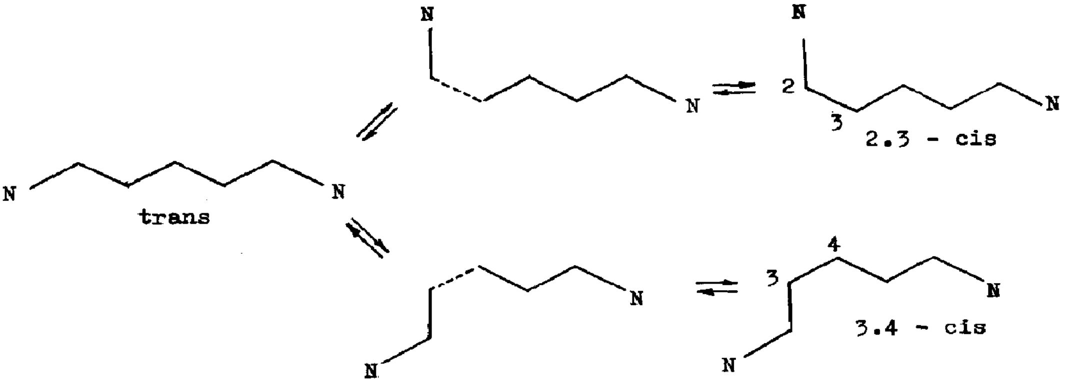

Fig. 3. Schematic diagram of the isomerization of pentamethinecyanine.

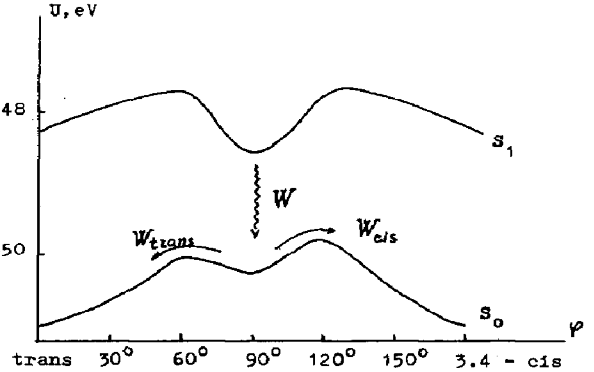

Fig. 4. Potential energy curves of the trans–cis isomerization of pentamethinecyanine in a polar medium (water) as a function of the torsion angle φ [8].

A significant effect of the polar medium is the decrease of the energy barrier $\tilde{U}_0$ (Fig. 1). The barrier for rotation around the 2—3 bond (about 80 kJ mol^{-1}) is higher than that for rotation around the 3—4 bond (about 40 kJ mol^{-1}). Therefore the second pathway should be preferred.

The rate constant of the radiationless transition $S_1 \rightsquigarrow S_0$ resulting from the non-adiabatic interaction proportional to the velocity of the torsional motion requires to be calculated. As has been mentioned, the potential surface of the ground state of polymethine dyes in the gas phase has a maximum at $\varphi = 90°$. The following inequality is a necessary condition for the application of the proposed method (*i.e.* the introduction of an aggregate coordinate Q for the solvent):

$$\Omega_s \ll \tau_v^{-1} \qquad (15)$$

where Ω_s is the torsion frequency in the medium and τ_v is the time required to establish a partial equilibrium over all the degrees of freedom of the solvent except Q. When this condition is obeyed eqn. (8) can be used to describe the deactivation of the photoexcited state. It should be noted that this equation is an exact dynamic equation which does not imply any relation between the frequency Ω of the intramolecular motion and the rate τ_s^{-1} of solvent relaxation, as is also the case for the equation proposed by Zusman [19] (see also ref. 21).

Since $\tau_v^{-1} \approx 10^{13}$ s^{-1} [22] (*i.e.* τ_v is much less than τ_s) and the estimated value of Ω in the gas phase is about 3×10^{13} s^{-1}, the inequality (15) means that a high viscosity situation ($\Omega \ll \beta$) exists [1] (β is the viscous drag coefficient and is assumed to have a value of about 10^{14} s^{-1}).

It is necessary to determine the parameters E_r and Δ_{eff} in order to use eqn. (12) to calculate the probability of radiationless transition at $\varphi = 90°$. At 90° torsion the structure is characterized by charge transfer from one part of the molecule to the other. The polymethinic fragment is uncharged in the ground state whereas the polyenic fragment bears a positive charge; however, in the S_1 state the polymethinic fragment at $\varphi = 90°$ has a positive charge $+e$ whereas the polyenic fragment is uncharged (Fig. 5). The charge redistribution caused by the electronic transition $S_1 \rightsquigarrow S_0$ at $\varphi = 90°$ can be approximately described as a transfer of the elementary charge from the centre of the polymethinic fragment to the centre of the polyenic fragment. In the metallic sphere model the reorganization energy E_r and the relative solvation energy Δ'' are [23]

$$E_r = e^2\left(\frac{1}{n^2} - \frac{1}{\epsilon}\right)\left(\frac{1}{2a} + \frac{1}{2b} - \frac{1}{r}\right) \approx 3.4 \text{ eV}$$

$$\Delta'' = e^2\left(1 - \frac{1}{\epsilon}\right)\left(\frac{1}{2b} - \frac{1}{2a}\right) \approx 0$$

where a and b are the radii of the polymethinic and polyenic fragments respectively ($b \approx a \approx 1.4$ Å [8]), r is the distance between their centres ($r \approx 3.5$ Å [8]), n is the refractive index of the solvent and ϵ is the static dielectric constant (if the solvent is water $n^2 = 1.8$ and $\epsilon = 78$).

In the Debye model the solvent relaxation time is $\tau_s = \tau_D n^2/\epsilon$ [24] where $\tau_D = 0.85 \times 10^{-11}$ s is the Debye reorientation time for a single dipole in the medium. By using the potential curves [8] we find $2\Gamma_0 \approx 2$ eV and $\Delta_{\text{eff}} \approx 2$ eV, so that the activation energy U_0 (eqn. (13)) is about 15 kJ

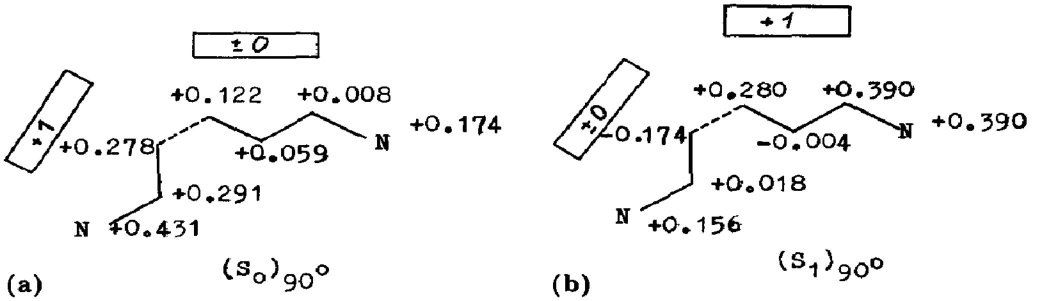

Fig. 5. π electron density distribution of (a) the ground state and (b) the first excited state of pentamethinecyanine twisted through 90° determined by means of a quantum-chemical calculation [8].

mol^{-1}. Then the rate constant of the radiationless transition $S_1 \rightsquigarrow S_0$ at $\varphi = 90°$ is

$$W \approx 2 \times 10^{10}\ \mathrm{s}^{-1} \tag{16}$$

where we have assumed $\omega_{\mathrm{eff}} = \min(\Omega, \tau_s^{-1}) = \tau_s^{-1} = 5 \times 10^{12}\ \mathrm{s}^{-1}$. The rate constant given by eqn. (16) corresponds to the formation of the transient (isomer) at $\varphi = 90°$ in the ground state. The rates of the transformations to the stable cis or trans forms are given by eqns. (14). At high viscosity ($\Omega \ll \beta$) the frequencies ω_a and ω_c in eqns. (14) are [20] $\omega_a = \Omega\Omega_a/2\pi\beta$ and $\omega_c = \Omega\Omega_c/2\pi\beta$, where Ω_a and Ω_c are the frequencies of vibration in the "upturn" potential near the barriers U_a and U_c respectively. According to ref. 8 $\Omega_a \approx \Omega_c \approx \Omega \approx 3 \times 10^{13}\ \mathrm{s}^{-1}$, $U_c \approx 50$ kJ mol^{-1} and $U_a \approx 20$ kJ mol^{-1}. Then the rate constants of the transition from the short-lived conformation at $\varphi = 90°$ to the trans and cis isomers are

$$\begin{aligned} W_{\mathrm{trans}} &\approx 7 \times 10^{8}\ \mathrm{s}^{-1} \\ W_{\mathrm{cis}} &\approx 3 \times 10^{3}\ \mathrm{s}^{-1} \end{aligned} \tag{17}$$

Estimates (16) and (17) are in qualitative agreement with the results of investigations of fast photoprocesses in polymethine dyes performed by Rentsch [2]. We assume the double-valley scheme suggested by Rentsch for the isomerization of streptocyanine dyes: the two valleys correspond to the potential minima of the trans isomer and the short-lived conformation at $\varphi = 90°$. Rentsch's experimental results for a number of polymethine dyes are

$$W^{(\mathrm{exp})} = (4.0 - 15.0) \times 10^{10}\ \mathrm{s}^{-1}$$

$$W_{\mathrm{trans}}^{(\mathrm{exp})} = (2.0 - 3.3) \times 10^{9}\ \mathrm{s}^{-1}$$

Acknowledgment

The authors would like to express their gratitude to Professor N. Tyutyulkov for stimulating discussions.

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