The temporal dipole moments of solute molecules undergoing charge transfer

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The expression for time dependence of excited state dipole moment of molecule with charge transfer on the correlation function of instant spectra kinetics has been deduced on the basis of the theory of solvatochromism. Time dependence of excited state dipole moment of well known luminescence probe 6-propionyl-2-dimethylaminonaphtalene in polar solvent is presented.

Keywords: time dependences, dipole moment, charge transfer.

1. Introduction

Until now the majority of researchers connects a redistribution of electronic density or charge transfer (CT) during excited state lifetime of some organic probes with different models, however, exact knowledge of the process is still unavailable. At the same time such a model would be the crucial point for right calculation of proper photoreactions and, therefore, the determination of CT mechanism is the problem of great practical importance. For proper choice of a model in all cases some more detailed study of kinetic characteristics of excited states is recommended.

Important conclusions about a geometrical transformation of molecular structure of quantum systems appearing in CT state could be obtained from the knowledge of its dipole moment change in time. The values of dipole moments of CT system in the S_1 state may be large enough and CT process is well known to be accompanied by a growth of excited state moments during its lifetime τ. It is worth to note, that available experimental methods allow us to obtain only stationary values of dipole moments for both the locally excited and CT states.

Here we deduce the dependence of $\mu(t)$ for a solute with charge transfer in the excited state on the bases of known correlation functions of instant spectra kinetics and widely used representations about mechanisms of solvatochromic phenomena (theory of Kawski [1]). The example of calculated time dependence of excited dipole moment is presented for molecules of 6-propionyl-2-dimethylaminonaphtalene (PRODAN) at the Stokes excitations of singlet excited states.

2. Deductions of the main equations

The solvatochromic shifts of the maximum in absorption $\tilde{\nu}_a$ and fluorescence $\tilde{\nu}_f$ are often described by equations of Bilot–Kawski [1, 2] in the following way:

$$\tilde{\nu}_0 - \tilde{\nu}_f = \frac{1}{4\pi\varepsilon_0} \frac{2}{hca^3} \left[(\mu_e - \mu_g)^2 f(\varepsilon, n) + \left(\mu_e^2 - \mu_g^2\right) f(\varepsilon, n) + 2\left(\mu_e^2 - \mu_g^2\right) g(n) \right]$$
(1a)

$$\tilde{\nu}_0 - \tilde{\nu}_a = \frac{1}{4\pi\varepsilon_0} \frac{2}{hca^3} \left[-(\mu_e - \mu_g)^2 f(\varepsilon, n) + \left(\mu_e^2 - \mu_g^2\right) f(\varepsilon, n) + 2\left(\mu_e^2 - \mu_g^2\right) g(n) \right]$$
(1b)

where μ_g and μ_e are the dipole moments in the ground and excited state, respectively, a is the Onsager radius, and solvatochromic function $f(\varepsilon, n)$ is equal

$$f(\varepsilon, n) = \frac{2n^2 + 1}{n^2 + 2} \left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right)$$
(2)

while $g(n)$ is given in the form

$$g(n) = \frac{3}{2} \frac{n^4 - 1}{\left(n^2 + 2\right)^2}$$
(3)

Charge transfer process is accompanied by a change of dipole moment, which depends on time as a results a redistribution of electronic density, $\mu_e(t)$ and a shift of maximum of fluorescence frequency $\nu(t)$. Both processes are due to a movement of the system towards an equilibrium state and, therefore, after simplification the Eq. (1a) may be written as

$$\tilde{\nu}_0 - \tilde{\nu}_f(t) = \kappa \left\{ \left[f(\varepsilon, n) + g(n) \right] \mu_e^2(t) - f(\varepsilon, n) \mu_g \mu_e(t) - g(n) \mu_g \right\}$$
(4a)

On other hand, for the ground state, we also can assume that arriving of a solute from CT to Franck–Condon state is accompanied by a creating of dipole moment, which differs from the steady state value μ_g. Therefore, we can also treat the ground state dipole as time dependent, $\mu_g(t)$, and then the Eq. (1b) may be presented as

$$\tilde{\nu}_0 - \tilde{\nu}_a(t) = \kappa \left\{ -\left[f(\varepsilon, n) + g(n) \right] \mu_g^2(t) + f(\varepsilon, n) \mu_e(0) \mu_g(t) - g(n) \mu_e^2(0) \right\}$$
(4b)

where $\kappa = 2/(4\pi\varepsilon_0 hca^3)$. The shifts of the maximum $\nu_{f/a}(t)$ in (4a) and (4b) can be described by the correlation function $C(t)$

$$C_{f/a}(t) = \frac{\tilde{\nu}_{f/a}(t) - \tilde{\nu}_{f/a}^{(2)}}{\tilde{\nu}_{f/a}^{(1)} - \tilde{\nu}_{f/a}^{(2)}} \tag{5}$$

The Equations (4), taking into consideration $C_{f/a}(t)$ in agreement with Eq. (5), has an exact solution

$$\mu_{e/g} = \frac{1}{2} A_1 + \frac{1}{2}(A_2 \pm A_3)^{1/2} \tag{6}$$

where

$$A_1 = \frac{\mu_{g/e}}{1 + \dfrac{g(n)}{f(\varepsilon, n)}}$$

$$A_2 = \left[\frac{f(\varepsilon, n) + 2g(n)}{f(\varepsilon, n) + g(n)} \right]^2 \mu_{g/e}^2$$

$$A_3 = \frac{4}{\kappa f(\varepsilon, n) \left[1 + \dfrac{g(n)}{f(\varepsilon, n)} \right]} \left\{ \tilde{\nu}_{f/a}^{(0)} - \tilde{\nu}_{f/a}^{(2)} - C_{f/a}(t) \left[\tilde{\nu}_{f/a}^{(1)} - \tilde{\nu}_{f/a}^{(2)} \right] \right\}$$

For instant time of $t = 0$, $C(t) = 1$ the Eq. (6) takes the form

$$\mu_{e/a}(0) = \frac{1}{2} \left\{ \frac{\mu_{g/e}}{1 + \dfrac{g(n)}{f(\varepsilon, n)}} + \sqrt{ \left[\frac{f(\varepsilon, n) + 2g(n)}{f(\varepsilon, n) + g(n)} \right]^2 \mu_{g/e}^2 \pm \frac{4 \left(\tilde{\nu}_{f/a}^{(0)} - \tilde{\nu}_{f/a}^{(1)} \right)}{\kappa f(\varepsilon, n) \left[1 + \dfrac{g(n)}{f(\varepsilon, n)} \right]} } \right\} \tag{7}$$

We assign value $\mu_e(0)$ to dipole moment of LE state and $\mu_g(0)$ – for non equilibrium, Franck–Condon dipole of the ground state. At instant time $t = \infty$, $C(t) = 0$, and we have from Eq. (6)

$$\mu_{e/g}(\infty) = \frac{1}{2} \left\{ \frac{\mu_{g/e}}{1 + \dfrac{g(n)}{f(\varepsilon, n)}} + \sqrt{ \left[\frac{f(\varepsilon, n) + 2g(n)}{f(\varepsilon, n) + g(n)} \right]^2 \mu_{g/e}^2 \pm \frac{4 \left(\tilde{\nu}_{f/a}^{(0)} - \tilde{\nu}_{f/a}^{(2)} \right)}{\kappa f(\varepsilon, n) \left[1 + \dfrac{g(n)}{f(\varepsilon, n)} \right]} } \right\} \tag{8}$$

Here we can identify $\mu_e(\infty)$ as dipole of CT state and $\mu_g(\infty)$ as equilibrium dipole of ground state. At $g(n) = 0$, the Eq. (6) will take the same form as in our recent papers [3–5], a difference is only in the shape of solvatochromic function $f(\varepsilon, n)$ as we use here another solvatochromic theory.

At the present time we have not experimental data which would let us to find a correlation function for absorption spectra. Therefore, in the next section we present only the dipole moment change in the exciting state neglecting a change of $\mu_g(t)$ in time, *i.e.*, treating μ_g as constant.

3. Analysis of the dipole moment in the excited state

The correlation function was fitted by using the data of time resolved fluorescence spectroscopy of PRODAN in glycerol at temperature $T = 293$ K and at the Stokes excitation at near $\lambda = 403$ nm [6]. The obtained correlation function can be approximated by the sum of two exponential curves with amplitudes and time constants: $a_1 = 0.998$, $\tau_1 = 668$ ps, $a_2 = 0.002$, $\tau_2 = 1370$ ps. The mean time of the instant spectra shift is equal 671 ps. The frequency of LE band maximum $\nu_1 = 21220$ cm^{-1} was taken as initial point at time $t = 0$. The frequencies of CT band maxima were treated as $\nu(t)$ and, at last, as the final value of relaxed spectra were taken value $\nu_2 = 18266$ cm^{-1}. The wavenumber of emission maximum of free molecules of PRODAN for the LE planar configuration, the ν_0, chosen for calculations was 26500 cm^{-1}, which corresponds approximately to luminescence spectra in nonpolar solution. The dipole moment of the ground state μ_g was taken to be 2.14 D in agreement with [7].

Decomposition $\mu_e(t)$

$\mu^{CT} = 8.14$ D

$\mu_1 = -0.762$ D $\tau_1 = 532$ ps
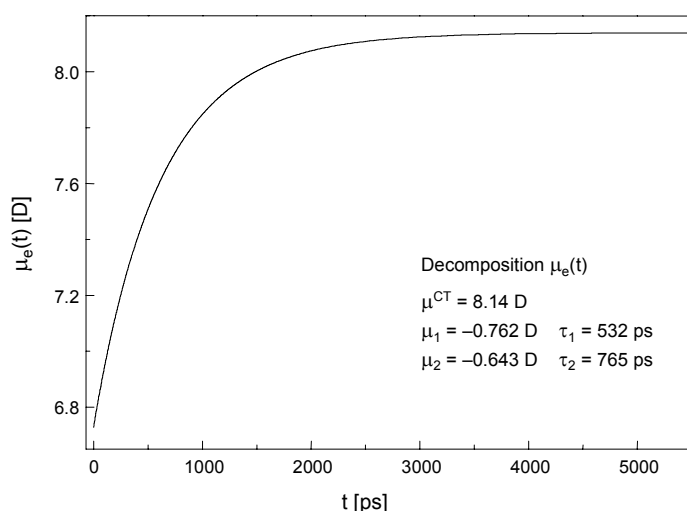
$\mu_2 = -0.643$ D $\tau_2 = 765$ ps

Figure. Time dependence of the dipole moment $\mu_e(t)$ of excited PRODAN in glycerol molecules calculated by formula (6).

The time dependence of the dipole moment is presented in the Figure. As it is seen there exists a fast growth of dipole moment from the value 6.73 D up to ~8.14 D during $t \sim 1500$ ps. Then, later, the second, slower interval between 1.5 and 5 ns is observed, where the absolute value of dipole reaches practically the maximum value 8.14 D.

The obtained $\mu_e(t)$ function may be approximated as the sum of the constant component $\mu_e(\infty)$ and two exponentially dependent components μ_1 and μ_2, the results of this fitting are presented in the right part of the Figure. Here, the mean time of dipole moment change equals to 660 ps. The obtained values of dipole moments $\mu_e(0)$, $\mu_e(\infty)$ are in reasonable agreement with the results received by KAWSKI *et al.* [7, 8], $\mu_e = 6.65$ D (thermochromic shift method) and $\mu_e = 6.4$ D (solvatochromic shift method) which were achieved on the base of the mean of steady state spectroscopy.

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