The Temporal Dipole Moment of Solute Molecules Undergoing Charge Transfer

V. I. Tomin and A. Krzysztofowicz

Institute of Physics, Pomeranian Pedagogical University,
76-200 Slupsk, Arciszewskiego str. 22B, Poland

Reprint requests to Prof. V. I. T; Tel/Fax: (1033)-59-8405-339, E-mail: tomin@pap.edu.pl

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Dedicated to Professor Jozef Heldt on the occasion of his 70th birthday

Important information about a geometrical transformation of solute molecules undergoing charge transfer in the excited state could be obtained from the knowledge of its dipole moment change in time, while experimental methods allow to obtain only stationary values of dipole moments for both the local excited and the charge transfer states.

On the basis of the theory of solvatochromism the relation for a time dependence of dipole moment on the correlation function for instant spectra kinetics has been deduced. Time dependence of the electric dipole moment of dimethylaminobenzonithryle in a polar solvent is presented. The initial and the final values of the dipole moments are close to those obtained by means of stationary spectroscopy methods.

Key words: DMABN; Dipole Moment; Luminescence; Local-excited and Charge Transfer States; Intermolecular Relaxation.

1. Introduction

Almost 40 years ago the dual luminescence of some organic systems was discovered [1], and since that time dozens of papers have been devoted to its various aspects. Dual luminescence is attributed to charge transfer (CT) connected with intramolecular redistribution of the electronic density. CT arises from originally populated local excited (LE) states, from which the excitation energy is transmitted by configurational changes of the molecule to the state with minimal internal energy. These radiationless transitions occur during the lifetime of the excited emitting state. In case of a free molecule such a transition is purely intramolecular. In polar solvents, however, it is strongly influenced by interactions with the molecules of the solvent. Hence, this process depends on the physical microstructure of the solution and its dynamics. Characteristically, molecules which undergo transitions from the LE state to the CT configuration show distinct changes of the luminescence spectra [2 – 4]. The emission from the CT state appears at longer wavelengths than that from the LE state. In polar solvents the differences between these two bands of the most sensitive molecules reach 100 – 120 nm, depending on the solvent.

Most researchers have ascribed the dual luminescence to two different mechanisms of electronic charge transfer. Exact knowledge of the mechanism would anable right calculations of photoreactions with CT participation and therefore the knowledge of the charge transfer mechanism is of great practical importance [2].

For a proper charge transfer model a detailed study is required. One of the essential characteristics is the electric dipole moment which determines the solvatation energy of the electronic state.

The CT process is well known to be accompanied by a growth of the electric dipole. For example, the dipole moment of the well studied dimethylaminobenzonithrile molecule increases during the lifetime of the S_1 state from 6-7 D in the ground state to 16-17 D in the equilibrium CT state [2, 5].

Recently, the model of inhomogeneous broadening (IB) of electronic spectra has been used for the description of photoprocesses with participation of CT in solutions [6, 7]. Different stages of CT have been treated as states of an IB, taking into account the contribution of thermal fluctuations of the solvate structure to the spectral position of the 0-0 transitions of a solute. IB is necessary for the explanation of a number of new results obtained by means of selective spectroscopy methods [8, 9], such as the bathochromic shift of spectra and a growth of the polarisation degree up to limit values at the far antiStokes excitation, the directed nonradiative energy transfer over inhomogeneous broadening states in ensembles of chemically identical molecules, and some others. To apply the IB model it is necessary to obtain a detailed knowledge of the excited dipole moment of the CT solute during the relaxation process over different states of IB, i. e. its temporal dependencies.

In the present paper we calculate the dependence of $\mu(t)$ of a solute with charge transfer in the excited state on the basis of the known correlation function and broadly accepted mechanisms of solvatochromic phenomena.

2. Deduction of the Main Equation

One of the methods of excited state investigation is connected with the analysis of the correlation function plotted on the basis of registered instant luminescence spectra [10]. If the frequency of the emission maximum of the solute shifts from ν_1 up to ν_2 during the luminescence lifetime, the correlation function may be written as

$$C(t) = \frac{\nu(t) - \nu_2}{\nu_1 - \nu_2}, \tag{1}$$

where the frequency $\nu(t)$ corresponds to the emission maximum at time t. As follows from (1), $\nu(t)$ depends on the correlation function $C(t)$:

$$\nu(t) = C(t)(\nu_1 - \nu_2) + \nu_2. \tag{2}$$

Simultaneously, in agreement with modern theories of solvatochromism [8, 11], the frequency of the luminescence maximum of a solute molecule depends on the local electric field intensity R interacting with the electric dipole of a solute and may be written as

$$\nu(R) = \nu_0 - \frac{\Delta\mu}{h}R, \tag{3}$$

where ν_0 is the frequency of the luminescence maximum of a free molecule of a solute, $\Delta\mu = \mu_e - \mu_g$, and μ_g and μ_e are the electric dipole moments of the solute in the ground and excited state, respectively.

Generally, $\Delta\mu$ depends on time due to the relaxation of the electronic states during the lifetime τ, and therefore it must result in a temporal change of the luminescence frequency

$$\nu(t) = \nu_0 - \frac{\Delta\mu(t)}{h}R. \tag{4}$$

Besides, R changes in time, mainly due to the polarising action of the excited dipole moment. That is why one may write

$$R(t) = f\mu_e(t). \tag{5}$$

As a result, by comparing the frequencies of emission from equations (2), (3) and taking into account the time dependencies (4) and (5) we obtain the relation

$$C(t)(\nu_1 - \nu_2) + \nu_2 = \nu_0 - \frac{\Delta\mu(t) f\mu_e(t)}{h}. \tag{6}$$

Let us assume that the change of the dipole moment in the excited state can be expressed by

$$\mu_e(t) = \mu_e^0 + \Delta\mu_e(t), \tag{7}$$

where μ_e^0 is the Franck-Condon value of dipole moment and $\Delta\mu_e(t)$ is the time dependent increase of the dipole moment in the excited state, which can be written as

$$\Delta\mu_e(t) = \mu_e(t) - \mu_e^0. \tag{8}$$

Usually, the dipole moment grows during the lifetime of the excited state owing to the LE → CT transitions up to the equilibrium values ${\mu_e}^{(2)}$, which for some CT molecules studied [2, 5] may be considerably larger than μ_e^0.

For the sake of simplicity we choose a case where the electric dipole of the ground state does not depend on time and is equal to the Franck-Condon value μ_e^0

$$\mu_g(t) = \mu_g(0) = \mu_g = \mu_e^0. \tag{9}$$

Then, due to the Eq. (7) – (9), (6) can be rewritten as

$$C(t)(\nu_1 - \nu_2) + \nu_2 = \nu_0 - \frac{(\mu_e(t) - \mu_g) f\mu_e(t)}{h}, \tag{10}$$

$$C(t)(\nu_1 - \nu_2) + \nu_2 = \nu_0 - \frac{f}{h}[\mu_e^2(t) - \mu_e(t)\mu_g]. \tag{11}$$

Equation (11) is quadratic and has the exact solution

$$\mu_e(t) = \frac{1}{2}\Big\{\mu_g + \Big[\mu_g^2 - 4\frac{h}{f}[(\nu_2 - \nu_0) + C(t)(\nu_1 - \nu_2)]\Big]^{1/2}\Big\}. \tag{12}$$

The values of ν_1 and ν_2 in (12) should be taken from instant spectra kinetics, and the frequency ν_0 may be evaluated from the absorption and luminescence spectra in a nonpolar solution or in the vapour phase. Quantum chemical calculations of the total energies of electronic states in a free state and in solvents could provide the necessary information concerning these values as well. The factor f can be calculated with the help of Onsagers model.

The simple relation (12) between $\mu(t)$ and $C(t)$ enables us to analyse the function of $\mu_e(t)$ and to draw some general conclusions. As follows from (12), it is easy to evaluate the change of the dipole moment due to charge transfer. Thus, for $t = 0$, when the correlation function $C(t) = 1$, the initial, the Franck-Condon value of the moment is given by

$$\mu_e(0) = \frac{1}{2}\left[\mu_g + \sqrt{\mu_g^2 + 4\frac{h}{f}(\nu_0 - \nu_1)}\right]. \quad (13)$$

From (13) one can see that the initial value of dipole moment in the excited state $\mu(t)$ depends, first of all, on the dipole moment magnitude in the ground state μ_g. Besides, it is important to know the value of the difference $\nu_0 - \nu_1$ which represents the solvatochromic shift of the CT emission.

For fully relaxed CT states $C(t)$ is zero and the dipole moment reaches the maximum value

$$\mu_e(\infty) = \frac{1}{2}\left[\mu_g + \sqrt{\mu_g^2 + 4\frac{h}{f}(\nu_0 - \nu_2)}\right]. \quad (14)$$

Evidently $\mu_e(\infty)$ is greater than $\mu_e(0)$. This is due to the time shift of luminescence instant spectra from ν_1 to ν_2.

3. Analysis of Temporal Dipole Moment

1. Temporal dependence of the dipole moment $\mu(t)$ occurs in the time interval in which a change of the correlation function $C(t)$ is noted. The following statement will also be true: if the correlation function is unchangeable during the lifetime τ, the excited dipole is constant and the dipole moment corresponds to the Franck-Condon one, i. e. CT doesn't take place.

2. The temporal behaviour of the $\mu(t)$ and the time correlation function $C(t)$ are not the same, and their decompositions will contain different components.

3. $\mu_e(0)$ and $\mu_e(\infty)$ are greater than the dipole moment of the ground state μ_g, and the increase of the moment, $\mu_e(\infty) - \mu_e(0)$, depends on the Stokes shift of emission maximum, i.e. $\nu_1 - \nu_2$.

We have taken for the analysis the correlation function $C(t)$ presented in Fig. 1, using the data of time resolved fluorescence spectra of DMABN in glycerol triacetate at $T = 283$ K and the Stokes excitation at the maximum of the absorption band near $\lambda = 302$ nm [10]. The frequency of the instant spectral maximum was chosen as relaxation parameter. The frequency of the LE band maximum $\nu_1 = 27540$ cm^{-1}, is taken to occur at the time $t = 0$. Then, for $t = 50$ ps, when the charge transfer band is well seen, the frequencies of the CT band maxima are treated as $\nu(t)$ and, at last, as the final value $\nu_2 = 21750$ cm^{-1}, the frequency of the CT band is maximal at $t > \tau_e$. This correlation function is multiexponential with time constants in pico-, subnano- and nanosecond time scales. The wavenumber of the emission maximum ν_0 of free DMABN molecules for the LE planar configuration, chosen for the calculations, is 28500 cm^{-1}, which corresponds approximately to the luminescence spectra in a nonpolar solution. The dipole moment μ_g of the ground state is taken to be 6.6 D, in agreement with [5, 12, 13].

The dipole moment $\mu_e(t)$ calculated by means of (12), using the correlation function from Fig. 1, is shown in Figure 2. The factor f is calculated with the Onsager model:

$$f = 2(\varepsilon - 1)/(2\varepsilon + 1)a^3, \quad (15)$$

where a is the Onsagers radius, which is equal to 0.45 nm, like in [5]. The stationary value of ε for triacetine is 7.3.

One can see from Fig. 2 (see curve 1) that in this case there exists a fast growth of the dipole moment from ~ 9 D (close to the Franck-Condon one) up to ~ 15 D at t ~ 100 ps, and an other, slower one in the interval between 300 and 1000 ps, where the absolute value of dipole moment reaches the value of 15.8 D close to the maximum. Finally, within the time interval $1-4$ ns, $\mu_e(t)$ slightly rises, reaching a stable value of 16 D.

The obtained $\mu(t)$ function may be approximated by the sum of a constant component $\mu(\infty)$ and three exponentially dependent components μ_1, μ_2 and μ_3. The results of this decomposition are presented on the right bottom of Figure 2. The constant component $\mu(\infty)$ corresponds to the dipole moment in the CT state, μ_{CT}.

The accuracy and the behaviour of the $\mu_e(t)$ curve depend on the frequency ν_0, and to evaluate this factor

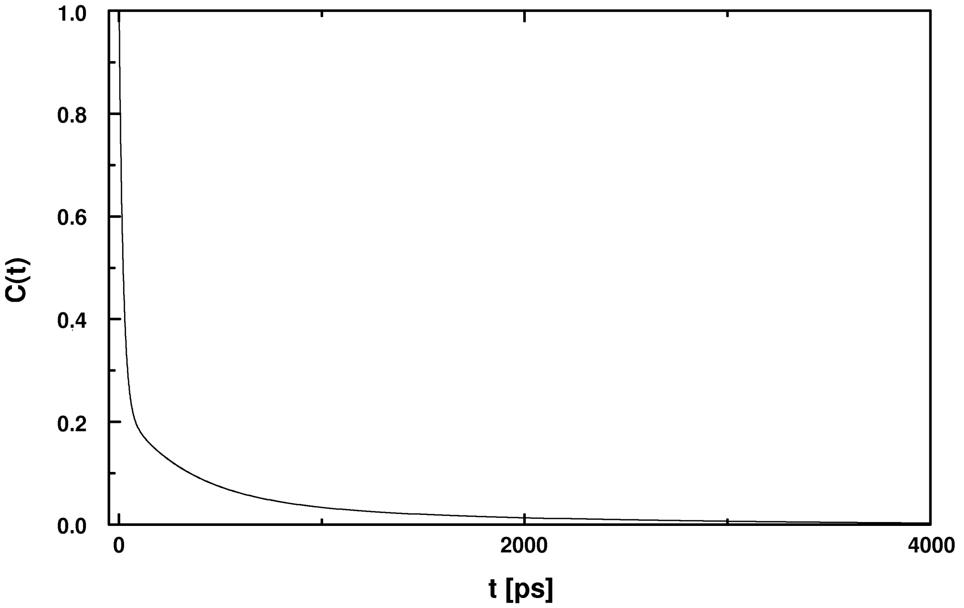

Fig. 1. The correlation function $C(t)$ of DMABN in triacetine at Stokes excitation near 302 nm, $T = 283$ K.

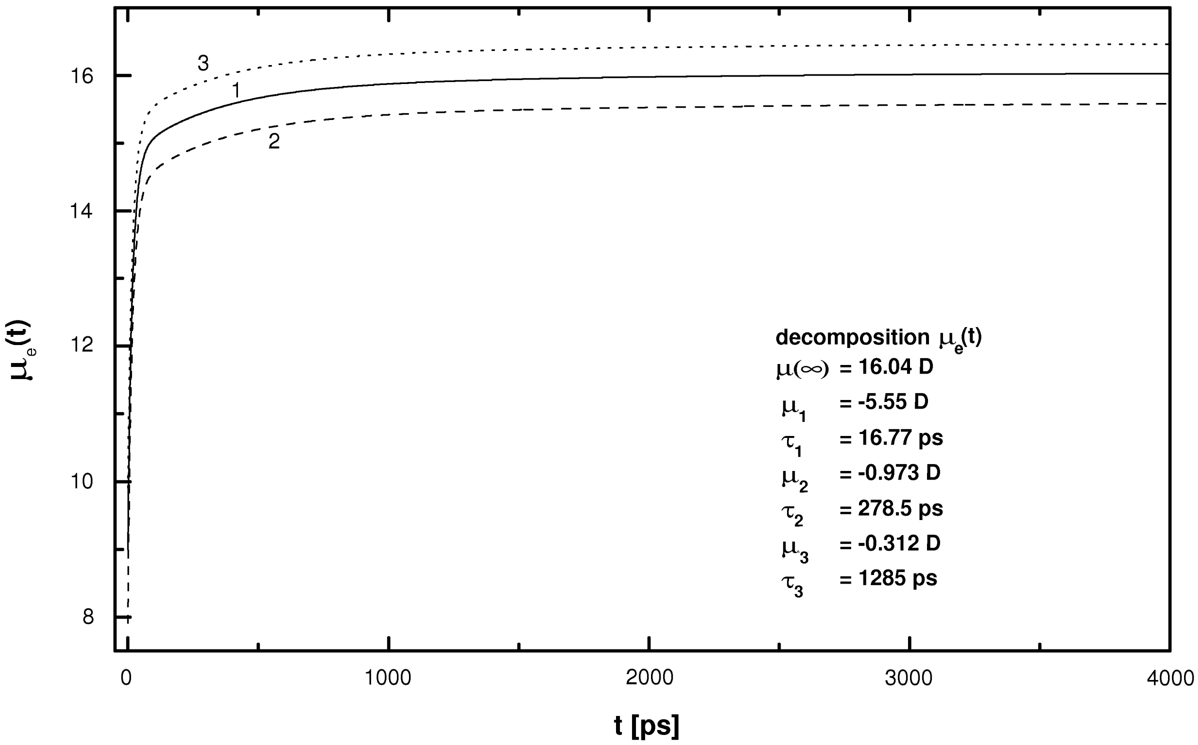

Fig. 2. The time dependences of the excited state dipole moment $\mu(t)$ of DMABN calculated with (12), using the correlation function $C(t)$ in Fig. 1 for the wavenumbers $\nu_0 = 28500$ cm^{-1} (curve 1), 28000 cm^{-1} (curve 2), and 29000 cm^{-1} (curve 3). The $\mu(t)$ function decompositions μ_1, μ_2 and μ_3 are exponentially dependent components; μ_∞ is a constant component corresponding to the dipole moment in the CT state, μ_{CT}.

Table 1. Stationary dipole moments, in Debays, of LE and CT excited states of DMABN. Different mechanisms of charge transfer are given in brackets: TICT – Twisted Internal Charge Transfer, RICT – Rehybridized Internal Charge Transfer.

Moment	Present paper	Experimental data [13]	Experimental data [5]	Theory [14]	Theory [12]
$\mu_e(0)$	8.5	10	5.7	6.9	8.9(gas phase) 9.9(cyclohexane) 12.4(acetonitrile)
$\mu_e(\infty)$	15.7	17	16.5	14.7 (TICT) 16.4 (RICT)	12.4(gas phase) 14.4(cyclohexane) 18.1(acetonitrile)

we calculated $\mu_e(t)$ curves for the frequencies 28500 ± 500 cm^{-1} as well. The corresponding curves 2 and 3 are presented in Fig. 2, which shows that such a dispersion of the frequency ν_0 leads to changes of $\mu_e(0)$ of 0.8 – 1.0 D and $\mu_e(\infty)$ of ~ 0.5 D.

The obtained dipole moments and those taken from the other sources for both emission bands are presented in Table 1. The final values of the dipole moments, $\mu_e(\infty)$, correspond (within the accuracy of the experimental methods) to those for the CT band obtained in [5, 13] for DMABN on the basis of the data of stationary spectroscopy, $\sim 16.5 - 17$ D and agree well with the mean data of different methods of quantum chemical computer calculations $\sim 15 \pm 3$ D. We ascribe the initial value of $\mu(t)$, 8.5 D, to the LE band of emission. This value agrees also well with experimental data and theory, from 5.7 up to 10 D, respectively. A more detailed comparison may be performed taking into account the following factors: (i) inaccuracies in the determination of emission frequencies due to broad bands of emission and uncertainties of corrected spectra of emission, (ii) incorrectness of dipole moment measurements in different solvents and (iii) approximation of the luminophor solvate with Onsager sphere model, which is not the best approach to reality.

4. Conclusions

1. On the basis of the theory of solvatochromism the expression (12) has been deduced. It describes the temporal dependence of the excited dipole moment on the correlation function of instant spectra kinetics. The obtained relation is quite general and has been received without applying any definite model of solution structure.

2. The verification of relation (12) has been carried out for DMABN in polar solutions. The initial $\mu_e(0)$ and final, relaxed $\mu_e(\infty)$ values of dipole moments correspond to those calculated for local excited, ${\mu_e}^{LE}$, and charge transfer, ${\mu_e}^{CT}$, states obtained by means of theoretical methods and stationary spectroscopy data. This circumstance allows us to conclude that the proposed method of dipole moment determination can give both the right character of the dependence and absolute values of dipoles for excited states, whereas available experimental methods make it possible to obtain only stationary values of dipoles.

3. We believe that the knowledge of temporal dipole moment $\mu(t)$ can be applied to obtain a geometrical transformation of the molecular structure during charge transfer.

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