Anomalous Inhomogeneous Broadening of Electronic Spectra of Molecules with Internal Charge Transfer

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Z. Naturforsch. **58a,** 529 – 536 (2003); received March 18, 2003

Excited states with internal charge transfer of some molecules show an anomalously strong inhomogeneous broadening of their electronic spectra. Here such an inhomogeneous broadening for N, N-dimethylaminobenzonithrile (DMABN) was studied. The spectral inhomogeneity for DMABN in some polar solvents reaches 140 – 150 nm.

The interpretation of the obtained results is based on treating a solution as a set of chemically identical solvates with a luminophor molecule in the centre, having different energies of the pure electronic transitions. The inhomogeneity arises due to an intermolecular effect of the luminophors environment on its spectra in polar solvents, as well as a process of intramolecular movement of the twisting fragments relative to the main moiety of DMABN.

Key words: DMABN; Luminescence, Local-excited and Charge Transfer States; Inhomogeneous Broadening, Intermolecular Relaxation.

1. Introduction

Luminescent molecules have often been used as probe molecules in studies of the pH, polarity, oxygen concentration, viscosity and membranes of biological systems [1 – 4]. The luminescent light of the probe molecule is a very sensitive function of its environment.

Luminescent probes with complex multifunctional properties promise to be very interesting and useful in natural sciences in the coming years. The greatest interest is in molecules with a significant change of polarity on excitation, and creating both local-excited (LE), and charge transfer (CT) states [2, 3]. As a rule they possess two well-resolved luminescence bands, all their parameters being very sensitive to the environment. This enables monitoring an emission and its change over two parallel channels. Such objects may be molecules with atomic groups changing their orientation in an excited luminescent state (twist groups): N,N-dimethylaminobenzonithryl (DMABN) and relative dialkilines, aromatic sulfons (DMABS), prodan, laurdan and many other compounds, the study of which attracts a great deal of attention nowadays [3 – 5].

Dual luminescence is directly attributed to the presence of conformationally twisted CT states connected with intramolecular charge transfer. Their excitation arises from originally exited LE states, from which the excitation energy is transmitted by configuration changes of the molecule to the state with minimal internal energy. It is usually considered that these radiationless transitions occur during the lifetime of the excited emitting state. For free molecules such a transition is purely intramolecular, however in polar solvents it is strongly influenced by interactions with the solvent molecules, forming solvates. Hence, this process depends on the physical microstructure as well as on its dynamics. Characteristically, molecules which undergo transitions from the LE to the CT configuration show distinct changes of the luminescence spectra [3 – 5]. The emission from the CT state appears at longer wavelengths than the emission from the LE band. In polar solvents the difference between these two bands of DMABN reaches up to 110 nm, depending on the solvent.

The two-band luminescence of DMABN (the structural formula is presented in the right corner of Fig. 1) was first described in [6]. Many papers have been devoted to its investigation. Therefore these molecules are classical objects for the demonstration of photophysical peculiarities due to internal charge transfer. In addition to that, it is well known, that DMABN

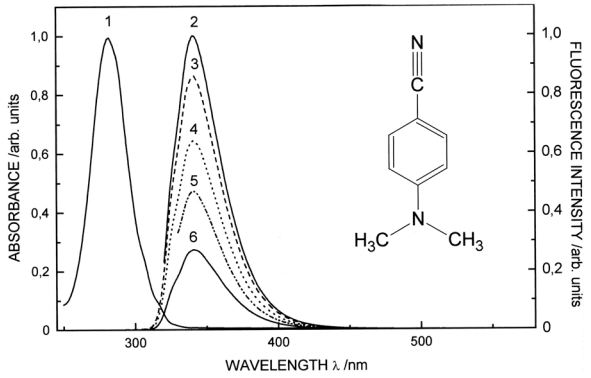

Fig. 1. Spectra of absorption **1** and luminescence **2** – **6** of DMABN in cyclohexane for various wavelengths of excitation: **2**: $\lambda_{ex} = 310$ nm, **3**: 260 nm, **4**: 270 nm, **5**: 320 nm, **6**: 280 nm.

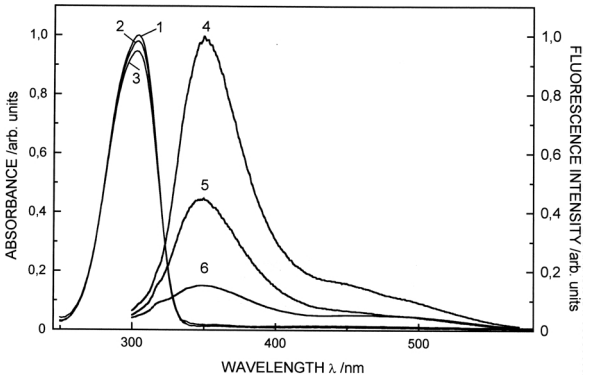

Fig. 2. Absorption **1** – **3** and luminescence **4** – **6** spectra of DMABN in glycerol at various temperatures: $\lambda = 260$ K **1**, **4**; 290 K **2**, **5**; 320 K **3**, **6**. Excitation wavelength: $\lambda_{ex} = 290$ nm.

changes its polarity during an electronic transition, so that the dipole moment grows from ~ 6 D in the ground state up to ~ 15 D in the CT configuration [5]. Hence, in polar solutions such luminophors show a strong sensitivity to solvatochromic effects and reveal spectral inhomogeneity due to the influence of the environment [2, 7], which may be both static and dynamic, as proposed in [7, 8]. This gives an additional important tool for explorations of interactions between the environment and luminescent molecules. The use of the dynamic model [2, 3, 7, 8] gives us a good possibility to study various molecular movements (both orientational and translational) in nano- and subnanosecond time ranges. In fact, a dependence of the ratio of the LE and CT forms on the energy of excitation, as well as a considerable change of the excitation spectra for different spectral ranges of registration, was observed in [9]. Thus one could anticipate that monitoring and studying the main characteristics of such inhomogeneous broadening in different solvents under various physical conditions facilitates the understanding of the photophysics of systems with internal charge transfer.

In this paper it is shown that DMABN molecules in polar solvents present an inhomogeneous system with unusual spectral characteristics, and that these characteristics can be interpreted.

2. Experimental Results

The spectroscopic studies were carried out on solutions of DMABN (Lancaster Synthesis) at concentrations of $10^{-6} - 10^{-4}$ M in the nonpolar solvents cyclohexane and glycerol at different temperatures. The luminescence spectra were registered on a HITACHI F-2500 spectrofluorimeter.

Figure 1 shows the longwavelength band of absorption and luminescence of DMABN in cyclohexane for various excitation wavelengths. In the symmetric band of absorption an impurity of a rather weak structure appears near 310 – 320 nm, the halfwidth being 25 nm. The luminescence spectrum shows only the local excited band at λ = 340 nm with the halfwidth $\Delta\lambda$ = 37 nm. It does not depend on the energy of excitation quanta at wavelengths from 270 up to 320 nm. The contour of the excitation band (not shown in the figure) does not point at any change within the range of luminescence from 320 up to 370 nm.

Figure 2 shows absorption and emission spectra for the same object in the polar solvent glycerol. As seen in this figure, the contour of absorption becomes more asymmetric and broader (the halfwidth $\Delta\lambda$ reaches 38 nm) at all temperatures indicated. DMABN in glycerol shows a relatively strong luminescence in the UV and the blue-green regions of the visible spectrum. At $T = 260$ K the short-wavelength LE component with maximum intensity at 350 nm is very strong. The other component is insignificant and appears as a shoulder at 460 nm. The maximum of the LE band in glycerol is shifted over 10 nm to the red compared to the same parameter of emission in the cyclohexane solution. Simultaneously, the contour of the band is broader than in cyclohexane, and its halfwidth is as high as 55 nm even in the solution at 260 K ($\Delta\lambda$ = 35 nm for cyclohexane). The integral emission power decreases with increasing temperature up to 330 K. A rather large broadening of the LE band halfwidth from 55 up to

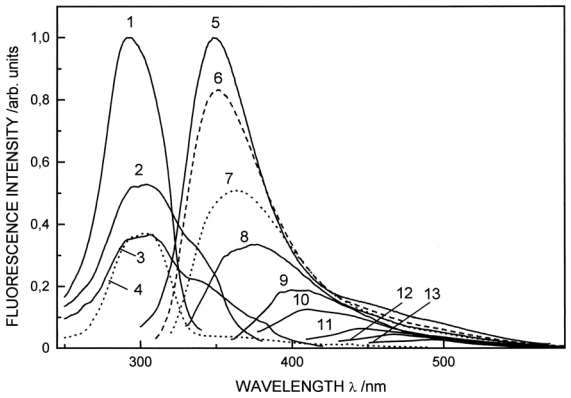

Fig. 3a. Spectra of luminescence excitation **1** – **4** and registration of various wavelengths **1**: $\lambda_{reg} = 350$ nm, **2**: 390 nm, **3**: 420 nm, **4**: 500 nm; and luminescence of DMABN **5** – **13** in glycerol obtained exciting the luminophor at λ_{ex} **5**: 290 nm, **6**: 300 nm, **7**: 310 nm, **8**: 320 nm, **9**: 350 nm, **10**: 370 nm, **11**: 390 nm, **12**: 410 nm, **13**: 430 nm. Temperatures: $T = 260$ K.

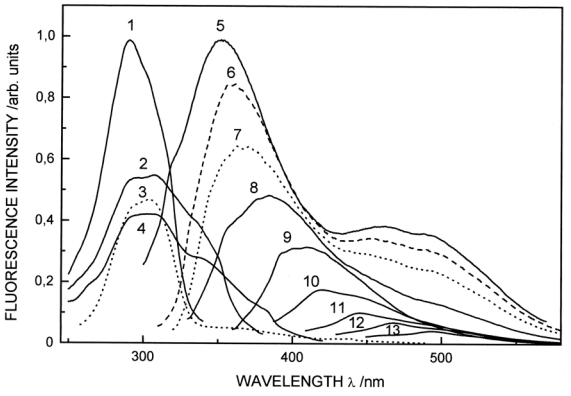

Fig. 3b. Spectra of luminescence excitation **1** – **4** and registration of various wavelengths **1**: $\lambda_{reg} = 350$ nm, **2**: 390 nm, **3**: 420 nm, **4**: 500 nm; and luminescence of DMABN **5** – **13** in glycerol obtained exciting the luminophor at λ_{ex} **5**: 290 nm, **6**: 300 nm, **7**: 310 nm, **8**: 320 nm, **9**: 350 nm, **10**: 370 nm, 11: 390 nm, **12**: 410 nm, **13**: 430 nm. Temperatures: $T = 330$ K.

77 nm is noted with heating of the solution up to 330 K. Actually, the growth of the temperature causes an increase of the relative intensity of the longwavelength component: The ratio $\mathbf{I_{LE}}/\mathbf{I_{CT}}$ decreases for the benefit of the CT band (here I_{LE} and I_{CT} are the intensities in the maxima of the LE and the CT luminescence band, respectively). The CT component is more essential (see Fig. 2) for temperatures close to 290 K, and at $T = 330$ K the emission band is already characterised by the second maximum of the spectrum at 460 nm.

The luminescence spectra at various excitation wavelengths and the spectra of emission excitation at various wavelengths are presented in Fig. 3 for frozen ($T = 260$ K) and heated ($T = 330$ K) solutions. The most interesting property of spontaneous emission of DMABN is the unusually strong dependence of its band on the wavelength of the exciting light in the range 290 – 380 nm. The character of changing concerns both emission bands and looks as follows: firstly, the ratio of the component intensities, the $\mathbf{I_{LE}}/\mathbf{I_{CT}}$, decreases, and later, at $\lambda_{ex} = 320$ nm the whole spectrum broadens and the band maximum shifts to the red edge by 12 nm; secondly, the subsequent reduction of the λ_{ex} affects the further shift of the spectra as a whole up to 495 nm at $\lambda_{ex} = 430$ nm. Hence, the overall drift of the spectra is anomalously large and equals 140 – 145 nm. It is unusual that the observed dependence takes place for higher temperatures $T = 330$ K as well (see Fig. 2b). The character of the shift for different temperatures is shown in Figure 4. Note that the dependence of the emission maximum deviates slightly from linear only at the beginning of the curves for the excitation wavelength in the range 310 – 370 nm.

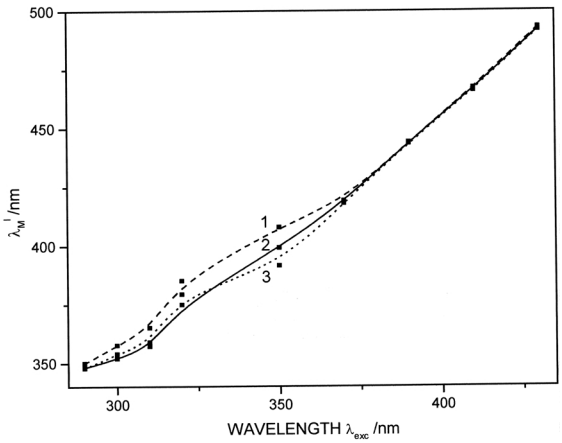

Fig. 4. Excitation wavelength dependencies of DMABN luminescence maxima for various temperatures (T values are for 1: 330 K, for 2: 260 K, for 3: 290 K).

The spectra of the luminescence excitation, also shown in Fig. 3 (curves 1 – 4), essentially depend on a wavelength of registration. The excitation spectra have one maximum near 290 nm when monitoring emission at $\lambda_{reg} = 350$ nm (the LE band). Characteristically, an additional structure appears in these spectra at regis-

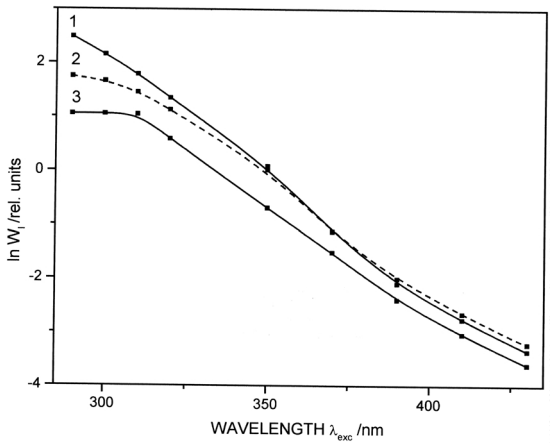

Fig. 5. The logarithm of the DMABN luminescence power dependence on the excitation wavelength: 1: 260 K, 2: 290 K, 3: 330 K.

tration in the range 390 – 420 nm. At a displacement of registration to the vicinity of 390 nm, the spectrum of excitation broadens due to the second maximum in the area 340 nm. More strongly a relative contribution of this maximum is seen at $\lambda_{\text{reg}} = 420$ nm. Further displacement of registration in the red part of the spectrum reduces the contribution of this absorption. Lastly, at $\lambda_{\text{reg}} = 500$ nm the basic band near 290 nm, similar to the curve 1 ($\lambda_{\text{reg}} = 350$ nm), is mainly seen in absorption, however it shifts slightly to the red edge of the visible range.

The dependencies of the logarithm of the spectrally integrated emission ($\ln W_{\text{lum}}$) on λ_{ex} are presented in Figure 5. As seen from this figure, the function of $\ln W_{\text{lum}}$ drops strongly and practically linearly from 2 down to -3(in relative units). The character of this change has approximately the same feature for all temperatures used.

In conclusion, it should be added that all registered red-edge excitation effects are noted for chosen concentrations in the diapason $10^{-6} - 10^{-4}$ M and in some other polar alcochols as, for instance, methanol and pentanol.

3. Discussion

Apparently there is no reason to disagree with the interpretation of the dual luminescence given by Grabowski, Lippert, and Rettig [4, 5]. According to these authors, short and long wavelength bands appear as transitions from the local excited S_1(LE) and the charge transfer S_1(CT) states, respectively. These two states correspond to two different conformations of the molecule skeleton and, consequently, to various distributions of the electronic energy density of the excited molecule. As a whole, this concept gives us an understanding of the origins and competition of the two basic bands of emission. At the same time, the spectral properties of such molecules in polar solutions should be treated applying a model accounting for broadening due to the configurational factors or site inhomogeneities [7, 8]. Such a model is known, in general, for molecules with a rigid skeleton, however it is not directly applied and discussed in detail for CT systems.

We see from Fig. 1 that in the nonpolar solvent cyclohexane the emission of DMABN shows only one shortwavelength LE band near 340 nm. A charge transfer process in the excited state is not likely to be energetically suitable for such systems; this fact is known also from previous studies [4, 5]. Further, the contour of this emission band does not depend on the excitation wavelength in the range 270 – 320 nm. Besides, the excitation spectra are the same for various wavelengths of emission registration λ_{reg}. Hence, there is not any inhomogeneous broadening of the electronic spectra in this nonpolar solvent. This statement is valid here, of course, for transitions in the LE electronic configuration, for which the planes of the dimethyl groups and the aromatic moiety of DMABN coincide. The situation for other nonpolar solvents (for example hexane [10]) is similar.

In glycerol, on the contrary, we observe two bands for DMABN emission, as seen from Figure 2. The second band at 469 nm is mainly formed, by the CT state emission. The intensity of this band is less than that of the LE band and grows essentially with temperature.

The presented data show the kinetic energy influence on intramolecular interactions inside DMABN and molecular reorganisation of its shell. These results agree well with the well-known classical concept that the LE→CT transitions are accelerated by collisions within molecules of the solvent or “cages” [5]. Similar results were observed for a variety of molecules possessing LE and CT states [4, 5], and for the same molecules dissolved in other solvents as well. The temperature stimulates intramolecular transitions, leading to charge separation and inducing the transitions LE→CT. Their probabilities grow over the thermal diapason under consideration. Simultaneously, the nonradiative transitions $S_1 \rightarrow S_0$ increase, showing the decrease of the quantum efficiency in both bands of emission.

The overall temperature broadening of the LE band emission halfwidth by 40% (from 55 up to 77 nm) indicates, to our mind, the appearance of some additional emitting states with various frequencies of the electronic transitions $S_0 \rightarrow S_1$. The nature of these states is probably quite complex, and we can state that this broadening arises only in polar solutions of DMABN. The halfwidth of the absorption in glycerol, $\Delta\lambda = 38$ nm, is larger than that in cyclohexane, $\Delta\lambda = 25$ nm, showing an additional absorption with other frequencies of pure electronic transitions ν_{el}. We may suppose that the mechanism of such absorption and emission changes can be attributed to inhomogeneous broadening of electronic spectra due to intermolecular universal interactions of dipole-dipole character [7, 8].

Figure 3 shows more interesting dependencies. The luminescence spectra recorded at various excitation wavelengths are essentially different. This testifies more directly that in DMABN solution several molecular forms (conformations) are present. Some of them have the absorption spectra shifted to the red. Therefore, if the concentration is high enough, they can be registered by the red edge excited luminescence. Also, if both emission bands are treated separately, one can note that the LE and the CT band are both red shifted with increasing excitation wavelength (see Fig. 4). This means that the DMABN solution is a typical spectrally inhomogeneous system. As is well known, the observed dependence of the luminescence spectrum on the excitation frequency is an experimental criterion for inhomogeneous broadening [11]. The data presented in Figs. 3 and 4 confirm this criterion. The inhomogeneous broadening appears in the range of both bands, which are connected with the S_1(LE) and the S_1(CT) states. The curves plotted in Fig. 3 evidently show the inhomogeneous character of the luminescent centres existing in glycerol.

The integral power of luminescence dependencies on λ_{ex}, plotted in Fig. 5 evidently could be explained accounting for a distribution of emitting luminiphors ρ_e over an inhomogeneous coordinate. This ρ_e function ought to contain λ_{ex} as a parameter. Hence, the $\ln W(\lambda_{ex})$ function gives us information about the distribution ρ_e as a function of λ_{ex}. We note that this distribution is maximum for electronic transitions close to ones determining excitation of the LE states.

Now, let us discuss the nature of the observed inhomogeneous broadening and its properties.

First of all, look at the dependence of the luminescence maximum on λ_{ex} at 260 K. At this temperature glycerol exists already as an almost frozen rigid matrix, for which the configuration relaxation time $\tau_{rel} \sim 100$ ns [12] significantly exceeds the DMABN lifetime in the excited S_1(LE) and S_1(CT) states $\tau_0 \sim 4$ and 5 ns, respectively [5]. Thus, our rigid solution is characterised by slow reorientation of molecules in the solvate:

$$\tau_{rel} > \tau_0. \tag{1}$$

For this case it is quite natural to assume that we observe the fluorescence emission of various states of inhomogeneous broadening of our solute. One can suppose that the character of IB is affected by the nonhomogeneity of frozen solvent shells of the DMABN.

However, heating glycerol solutions up to 330 K decreases the relaxation times, now $\tau_{rel} \sim 0.1$ ns [12], and the condition of fast reorientation is fulfilled:

$$\tau_{rel} < \tau_0. \tag{2}$$

This means, contrary to the previous case, that for the lifetime of the excited state, $\tau_0 \sim 3-4$ ns, the equilibrium distribution of solvates over the intermolecular coordinates is established. A configuration of solvent dipole molecules determines the reactive electric field R interacting with the dipole moment of a luminophor. Thus, as proposed in [7, 8], the value of R could be treated as a natural intermolecular coordinate, and that is why the relaxation time in inequalities (1) and (2) are a function of R, i.e. $\tau_{rel}(R)$. The spectral broadening in case (2) is homogeneous, and this means that the luminescence spectra should not depend on λ_{ex}. Unfortunately, as can be seen from the data presented in Figs. 3–5, this is not the case for our system. Hence, there should be an other mechanism of slow relaxation responsible for inhomogeneous broadening observed and the red edge excitation effects registered. In our opinion, it is logical to assume that the relaxation times describing the torsional movements of the dimethyl groups is slow in comparison to τ_0, and due to this the inequality (1) is fulfilled. We think that the mechanism of such relatively slow torsional movements may be affected by the dielectric friction due to interactions of dimethyl group charges with the large dipoles $\mu = 3.7$ D of glycerol molecules in solvate shells. Thus we come to the conclusion that, to explain the function $\lambda_{lum}(\lambda_{ex})$ presented in Fig. 4, it is worth taking into consideration the full configurational and intramolecular relaxation time $\tau_{rel}(R, \varphi)$. Here φ is the twisting angle between the planes of the dimethyl groups and the

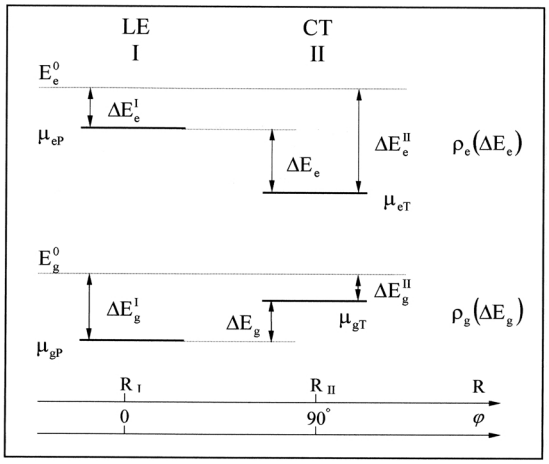

Fig. 6. Energetic diagram for the TICT molecule in solution. E_g^0 and E_e^0 are the electronic energy levels for a free molecule.

organic moiety of DMABN, which could be treated as an intramolecular coordinate for our luminophor. The equilibrium solvates are treated as having the minimal energies of external and internal interactions.

The mechanism of the observed red edge excitation effects (the $\lambda_{lum}(\lambda_{ex})$ is one of them) is connected with two principal phenomena:

(i) slow relaxation processes in comparison to the lifetimes of the excited states (condition(1));

(ii) principal factors giving spectral IB.

The first phenomenon (i) has been discussed already. For treating the second one (ii) it is natural to suppose and evaluate factors due to site inhomogeneities which, of course, are attributed to thermal fluctuations of solvate shells. We concentrate here on the simplest known 4 level scheme (see Fig. 6), which gives us the possibility to calculate the energies of the most important sublevels. The energetic level of a luminophor having the electric dipole moment μ in a solvent is shifted towards the energy of stabilisation, which is

$$\Delta E = -\mu \cdot R,$$

and, hence, the stabilisation energies of the principal states could be written in the form

$$\begin{aligned} \Delta E_g^I &= -\mu_{gP} \cdot R_I, \quad \Delta E_e^I = -\mu_{eP} \cdot R_I, \\ \Delta E_e^{II} &= -\mu_{eT} \cdot R_{II}, \quad \Delta E_g^{II} = -\mu_{gT} \cdot R_{II}, \end{aligned} \tag{3}$$

where μ_{gP} and μ_{gT} are the dipole moments in the ground, and μ_{eP} and μ_{eT} in the excited state for plane (P) and transverse (T) geometry, respectively. R_I and R_{II} are the intensities of the reactive electric fields corresponding to the equilibrium electric configurations of molecules in shells and dipoles μ_{gP} and μ_{eT} in the ground and excited states, respectively. They could be evaluated as in [8], using Onsagers sphere model with the radius a:

$$R_I = \mu_{gP} \cdot \chi, \quad R_{II} = \mu_{gT} \cdot \chi, \tag{4}$$

where susceptibility χ is expressed by

$$\chi = \frac{2(\varepsilon - 1)}{(2 \cdot \varepsilon + 1) \cdot a^3}. \tag{5}$$

One can find from (3)–(5) the difference between Franck-Condon and equilibrium sublevels for both states:

$$\Delta E_e = \chi \cdot \left(\mu_{eT}^2 - \mu_{eP}^2\right), \tag{6}$$

$$\Delta E_g = \chi \cdot \left(\mu_{gP}^2 - \mu_{gT}^2\right). \tag{7}$$

Taking into account the values for dipole moments and other parameters of DMABN [13] in glycerol: $\mu_{gP} = 6.15$ D, $\mu_{eP} = 5.7$ D, $\mu_{gT} = 4.05$ D, $\mu_{eT} = 16.5$ D, $\varepsilon = 26.3$, $a = 0.45$ nm, one obtains the following parameters of interest:

$$\begin{aligned} &\Delta E_e = 6180 \text{ cm}^{-1}, \quad \Delta E_g = 230 \text{ cm}^{-1}, \\ &R_I = 1.9 \cdot 10^7 \text{ V/cm}, \quad R_{II} = 5.14 \cdot 10^7 \text{ V/cm}. \end{aligned}$$

The values of the energy gaps ΔE_e and ΔE_g could be taken as values of broadening for the appropriate states, taking into account the dispersion of the thermal fluctuations ΔR of the internal field in agreement with formulas

$$\langle \delta E_e \rangle = 2\langle \mu_e \rangle \Delta R, \quad \langle \delta E_g \rangle = 2\langle \mu_g \rangle \Delta R, \tag{8}$$

where $\langle \mu_g \rangle = 0.5(\mu_{gP} + \mu_{gT})$ and $\langle \mu_e \rangle = 0.5(\mu_{eP} + \mu_{eT})$ are the average dipole moments in the ground and excited electronic states, respectively. The ΔR, as following from (8) could be written as

$$\Delta R = \sqrt{2\chi kT}. \tag{9}$$

From the expressions (8) and (9) we have $\langle \delta E_e \rangle = 1590 \text{ cm}^{-1}$ and $\langle \delta E_g \rangle = 740 \text{ cm}^{-1}$.

Hence, the overall spectral broadening of the $S_0 \rightarrow S_1$ transition is

$$\Delta\tilde{\nu} = (\Delta E_g + \Delta E_e + \langle \delta E_e \rangle + \langle \delta E_g \rangle)/hc. \tag{10}$$

Finally, using the expressions (1)–(10), for the possible total halfwidth we have $\Delta\tilde{\nu} = 8740\ \mathrm{cm}^{-1}$. If we apply the results obtained to the bands of DMABN in the scale of λ, the average spectral distance of various inhomogeneous states must be 154 nm; this agrees well with the indications of Fig. 4, where the overall shift of the emission maximum of 145 nm is noted.

Thus, the mechanism of inhomogeneous broadening due to site inhomogeneity has the same value as the one observed in our experiments. For TICT molecules ought to exist also the other mechanism, which appears owing to distributions of solutes over the twist angle φ and to the dependence of a pure electronic transition frequency on this angle. The experimental data, indicating the role of different conformations of the TICT molecular objects in dependencies on luminescence spectra and the excitation spectra, were reported in [14–16]. In paper [14] for laurdan, using quantum mechanical simulations it has been shown that the fluorescence band broadening is connected with the electronic transition frequency dependence $v_{\mathrm{el}}(\varphi)$ on the twisting angle φ. In solutions, this mechanism should be valid for all possible conformational states of DMABN as well. The definite function $v_{\mathrm{el}}(\varphi)$ could be obtained using dependencies of electronic energies S_0 and S_1 on the twist angle, $E_1(\varphi)$ and $E_2(\varphi)$; the ones known for these molecules [5]. The process of solvatation enhances the broadening of various conformational substates, and its value is tied directly and has the same order of magnitude as the broadening owing to configurational factors. As a result, a pure electronic frequency depends both on the intra φ and the internal R coordinates and may be presented as $v_{\mathrm{el}}(\varphi, R)$. The selective wavelength excitation of solution leads to a resonance population, mainly substates of inhomogeneous broadening, having maximal absorption on the λ_{ex}.

4. Conclusion

The results presented in this paper allow to make the following important conclusions.

1. Molecules of DMABN in polar solution exist as a set of various chemically identical forms. These forms have their own frequencies of pure electronic transitions $v_{\mathrm{el}}(\varphi, R)$. This means that DMABN in solution is a typical spectrally inhomogeneous system. The character of inhomogeneity can be defined as conformationally configurational. The inhomogeneous broadening covers the range of both bands, which are connected with the S_1(LE) and the S_1(CT) states. The broadening value registered is as high as 140–145 nm for glycerol solution. Such anomalously large values are due to the high change of polarity at an excitation $\Delta\mu$ and relatively small size of the luminophor molecules.

2. The spectral broadening can be calculated assuming dipole-dipole interactions and applying the Onsager model, if the values of the electric dipole moments in the excited and ground states are known. The formulas (1)–(10) give us the broadening order of $\Delta\tilde{\nu} \sim 8700\ \mathrm{cm}^{-1}$ or $\Delta\delta \sim 155$ nm.

3. To understand correctly the relaxation processes in solvates containing a luminophor in TICT states, it is necessary to take into consideration the full configurational and intramolecular relaxation time $\tau_{\mathrm{rel}}(R, \varphi)$ depending on the reactive field R and the twisting angle φ. The condition of inhomogeneous broadening should be slow reorientational relaxation over the R and φ coordinates $\tau_{\mathrm{rel}}(R, \varphi) > \tau_0$.

Acknowledgements

The authors are grateful to Prof. J. Heldt for permanent support, and to the Pomeranian Pedagogical University in Slupsk for partial financing of the project BW6/1239/02.

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