

Anomalous broadening of DMABN electronic spectra in solutions

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The results of spectral broadening study of electronic bands of an archetype molecule with intramolecular charge transfer in the excited state, *n*-dimethylaminobenzonitrile (DMABN), in polar solvents are discussed. The broadening is anomalously large, it amounts to 8000 cm^{-1} , and manifests itself in both luminescence and excitation spectra. The explanation of the results obtained is based on treating a solution as a set of chemically identical solvates with solute in the centre, which have different energies of the pure electronic transitions. The inhomogeneity is likely to arise due to both the intermolecular effect of luminophor environment on its spectra in polar solvents and the existence of various conformers of DMABN.

Keywords: DMABN, luminescence, local-excited and charge transfer states, conformers, relaxation.

1. Introduction

Nowadays, a great deal of interest is concentrated on molecules showing significant change of polarity during electronic transition upon excitation and having the ability to create both local-excited (LE) and charge transfer (CT) states [1–3]. It is well known that *n*-dimethylaminobenzonitrile (DMABN) changes its charge distribution during electronic transition, so that the dipole electric moment grows from $\sim 6\text{ D}$ in the ground state up to $\sim 16\text{ D}$ in the CT configuration [4]. Hence, in polar solutions such solutes must show a strong enough sensitivity to solvatochromic effects and reveal spectral inhomogeneity due to the influence of the environment [1–3, 5]. Indeed, the excited electronic states with internal charge transfer of some molecules show an anomalously strong inhomogeneous broadening of their electronic spectra as was firstly shown for laurdan [6]. Recently, spectral inhomogeneity characteristics of an archetype molecule DMABN in polar solvents were found by means of steady-state spectroscopy [7–9]. The inhomogeneity manifests itself in both luminescence and excitation spectra, and the spectral shifts of luminescence maximum with a change of excitation wavelengths are anomalously large and amount to 8000 cm^{-1} . Later, the results of kinetic study of

emission decay and polarization of DMABN long wavelength luminescence upon excitation on the red edge of absorption spectra near 403 nm were published [10–12]. Quantum mechanical simulations also evidence the existence of conformers with considerably different 0–0 frequencies. Neither of the results obtained in [6–12] does contradict the explanation that the observed inhomogeneity arises due to both the effect of solute environment on its spectra in polar solvents and the existence of its various conformers. However, the question: “What is the nature of CT probes electronic spectra?” has not been fully cleared up until now.

Here, we present some new results of the study of kinetic characteristics of DMABN forms emitting in the long-wave part of the spectrum to show, together with other data, that DMABN in polar solvents may be treated as an inhomogeneous system with unusual spectral characteristics.

2. Experimental

Excitation and emission spectra were registered on a HITACHI F-2500 spectrofluorimeter and HITACHI U-2010 spectrophotometer. The kinetic characteristics of luminescence were obtained using light pulses of 65 ps duration of a semiconductor laser at $\lambda = 403$ nm (24810 cm^{-1}). DMABN (Lancaster Synthesis, 99.9%) was used without further purification at concentrations of 10^{-6} – 10^{-3} M.

3. Results and Discussion

Luminescence spectra of different excitation wavelengths and the spectra of emission excitation registered at various wavelengths are presented in the Figure, for a solution in glycerol at room temperature (295 K). The standard excitation near maximum of absorption 34480 cm^{-1} is followed by a dual luminescence spectrum with maxima at 27780 and 22000 cm^{-1} . The first short wavelength band is referred to the LE, and the second long wavelength to the CT states. The halfwidth of LE band reaches 4600 cm^{-1} . The most interesting property of spontaneous emission of DMABN firstly reported in [7–9] is unusual well-pronounced dependence of its band on exciting light wave number ν_{ex} in the range of 34480 – 23260 cm^{-1} (3–6). The character of changing concerns both emission bands and as seen already at $\nu_{\text{ex}} = 28570$ cm^{-1} the whole spectrum broadens and the band maximum shifts to the red edge by 4000 cm^{-1} . A subsequent decrease of the ν_{ex} affects further shift of the spectra as a whole down to 20200 cm^{-1} at $\nu_{\text{ex}} = 23260$ cm^{-1} (6). Hence, for wave numbers lesser than 28570 cm^{-1} we observe a full “cut off” of the LE band. Such phenomena could be referred to the so-called red edge excitation effects (REEE) [5]. The overall drift of the emission spectra average frequency is anomalously large and equals 8000 cm^{-1} . It is unusual that the observed dependence takes place even at elevated temperatures $T = 330$ K, and in other solvents with lower viscosity as well.

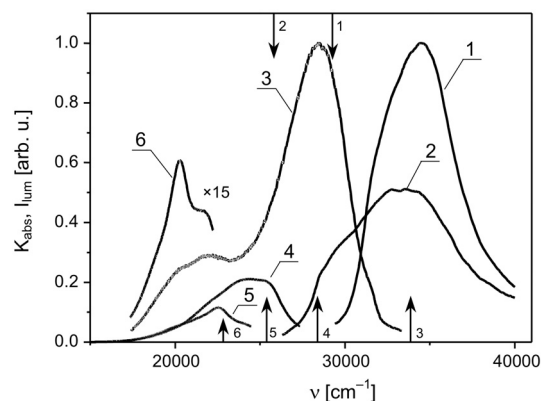


Figure. Spectra of excitation (1, 2) at wave number of registration 27780 cm^{-1} (1) and 20000 cm^{-1} (2) and luminescence spectra (3–6) of DMABN in glycerol for different excitation wave numbers: 34480 cm^{-1} (3), 28570 cm^{-1} (4), 25640 cm^{-1} (5) and 23260 cm^{-1} (6).

The spectra of the luminescence excitation, presented in the Figure (curves 1 and 2), essentially depend on the wave number of registration. As seen from curve 1, it has one maximum near 34480 cm^{-1} when monitoring emission at $\nu_{\text{rec}} = 28570\text{ cm}^{-1}$ (the LE band). However, at $\nu_{\text{rec}} = 20000\text{ cm}^{-1}$ (curve 2) not only the basic band near 34480 cm^{-1} , similar to that on curve 1, but also the intensive long wavelength shoulder are seen in the absorption.

It should be added that all red-edge excitation effects registered are noted for chosen concentrations in the range of 10^{-6} – 10^{-3} M and in some other polar protic and aprotic solvents such as methanol, pentanol, ethanol, tetrahydrofuran (THF) and acetonitrile (ACN). At the same time DMABN luminescence in nonpolar solvents (cyclohexane, n-hexane and so on) reveals only the LE band near $\nu = 29400\text{ cm}^{-1}$ with the halfwidth $\Delta\nu = 3200\text{ cm}^{-1}$, which is essentially less than that in polar glycerol ($\Delta\nu = 4600\text{ cm}^{-1}$). The contour of emission does not depend on the excitation in the region of 37040 – 31250 cm^{-1} .

We have studied DMABN emission temporal behavior when molecular species having spectra close to those presented in the Figure (curves 5 and 6) were excited by radiation of semiconductor laser at $\nu = 24810\text{ cm}^{-1}$. In Tab. 1 luminescence lifetimes are presented for registration in different spectral regions. As one can see deconvolution of luminescence pulses gives us three components in each case and their parameters depend on the wave number of registration. We consider as more reliable the second and third components with durations of ~ 1.2 and $\sim 5.4\text{ ns}$ (in glycerol). The average lifetimes $\bar{\tau}$ were also calculated for all the cases and they indicate definite dependence – the magnitude $\bar{\tau}$ of increases from ~ 2.7 up to $\sim 3.4\text{ ns}$ when the wave number drops in the interval 22220 – 18870 cm^{-1} . At the same time average lifetime at excitation of 33330 cm^{-1} is about 3.0 – 3.8 ns [4, 13] and is close to values obtained.

Table 1. Deconvolution of DMABN in glycerol emission decay pulses on the sum of three exponents; A_i and τ_i are the amplitude and time constant of the i -th component, $\lambda_{\text{ex}} = 403 \text{ nm}$ (24813 cm^{-1}), $C = 10^{-3} \text{ M}$.

Registration wavelength/wave number $\lambda_{\text{reg}}/\nu_{\text{reg}} [\text{nm}/\text{cm}^{-1}]$	Amplitudes and time constants of components							
	A_1	$\tau_1 [\text{ns}]$	A_2	$\tau_2 [\text{ns}]$	A_3	$\tau_3 [\text{ns}]$	χ^2	$\bar{\tau} [\text{ns}]$
450/22222	154608	0.045	10838	1.196	2986	5.106	1.59	2.66
490/20408	28150	0.4	15658	1.517	5580	5.385	1.48	3.11
510/19608	25542	0.183	15948	1.636	6313	5.33	1.45	3.46
530/18868	19010	0.19	12475	1.6	5830	5.07	1.21	3.43

Table 2. Deconvolution of DMABN in glycerol emission anisotropy pulses on the sum of three exponents; A_i and τ_i are the amplitude and time constant of the i -th component, $\lambda_{\text{ex}} = 403 \text{ nm}$ (24813 cm^{-1}). The data of the lowest line are taken from [15].

Registration wavelength/wave number $\lambda_{\text{reg}}/\nu_{\text{reg}} [\text{nm}/\text{cm}^{-1}]$	Amplitudes and time constants of components								
	$r(0)$	A_1	$\tau_1 [\text{ns}]$	A_2	$\tau_2 [\text{ns}]$	A_3	$\tau_3 [\text{ns}]$	χ^2	$\langle \tau_B \rangle [\text{ns}]$
470/21277	0.285	1.029	20.163	-0.639	14.267	1.691	0.112	0.998	24.39
490/20408	0.297	-0.052	4.518	0.951	0.121	0.419	26.184	1.086	26.38
510/19608	0.287	0.289	0.240	-0.089	3.799	0.283	23.256	1.274	24.05
530/18868	0.285	-0.235	6.236	1.972	0.051	0.598	13.020	1.095	14.37
526/19011	0.331	0.336	17.641						17.64

In Table 2, the results of anisotropy kinetics $r(t)$ analysis for various wave numbers of observation are presented for DMABN in glycerol. As is seen the function $r(t)$ in all the cases may be presented as a sum of three exponential components. For any wave number, except 18870 cm^{-1} , the longer component is within the limits of 20 to ~ 26 ns, and only at $\nu \sim 18870\text{ cm}^{-1}$ it is considerably smaller ~ 13 ns. On the contrary, the second component for the same wavelength is ~ 6.2 ns and it is essentially longer than for $\nu_{\text{reg}} = 20410$ and 19610 cm^{-1} , where it deviates from 3.8 to 4.5 ns. Remarkably, this initial anisotropy $r(0)$ does not depend on the wave number of registration and is the same, *i.e.*, ~ 0.3 , for all the wave numbers of the observation.

When use is made of a hydrodynamic model of Stokes–Einstein–Debye the Brownian rotation times $\langle \tau_B \rangle$ in the interval 20–25 ns (the longest component in deconvolution) correspond to rotating volumes with radii 1.1–1.3 nm, which are pretty higher of DMABN dimensions 0.4–0.5 nm [14]. Taking into account the diameter of glycerol molecules of about 0.3 nm, one can conclude that a rotating volume of a solvate is restricted by the size of the first coordinative sphere. Approximately the same times $\langle \tau_B \rangle \sim 17.6$ ns and, consequently, rotating volumes were obtained when the solute was excite at absorption maximum ~ 302 nm and emission registered near maximum of CT band 19010 cm^{-1} [15].

Inhomogeneity of electronic spectra, in principle, may be caused by different factors. DMABN is a well studied molecule and we can estimate anticipated spectral shifts due to solvatochromic phenomena for planar (P) and perpendicular (T) geometry of solute. Any parameters necessary to calculate these frequencies are known and using the Onsager approach and magnitudes for all dipole moments $\mu_{gP} = 6.15$ D, $\mu_{eP} = 5.7$ D, $\mu_{gT} = 4.05$ D and $\mu_{eT} = 16.5$ D and the radius of Onsager cavity $a \approx 0.45$ nm in agreement with results of [14], we have a value $\Delta\nu_c = 6500\text{ cm}^{-1}$ for energy difference between 0–0 frequencies of both conformers, P and T . This is a very important point which indicates possible mechanism for spectra broadening if the conformers of both types exist in a solution simultaneously. The existence of conformers having only CT band also follows from experiments [16] with so-called “pretwisted” forms of DMABN derivatives.

Of course, except for this there should be the broadening of electronic spectra due to the mechanism of thermal fluctuations [1–3, 5]. Contributions of this mechanism can be estimated with the help of formula from [1]. Using maximal difference between dipole moments $\Delta\mu = \mu_{gP} - \mu_{eT} \approx 10$ D we obtain the magnitude of broadening $\Delta\nu_f \approx 1600\text{ cm}^{-1}$. Therefore, the total possible broadening will be equal to the sum of conformational and fluctuational broadenings, thus we have $\Delta\nu_{\Sigma} = \Delta\nu_c + \Delta\nu_f \approx 6500\text{ cm}^{-1} + 1600\text{ cm}^{-1} \approx 8100\text{ cm}^{-1}$.

The experimental value of spectral shifts, as seen from the Figure is 8000 cm^{-1} , thus we may state a very good agreement of this value with our estimates. The important argument in favor of different conformers contribution also follows directly from quantum mechanical calculations of various DMABN geometries differing in twist angle φ between planes of dimethylamino groups and organic moiety (see [17] and references therein). The energy difference, ΔE of the S_0 and excited singlet states S_1

and S_2 , which determines the frequencies of the pure electronic transitions ν_{00} depends on the angle and changes with the angle more than on 3000 cm^{-1} .

4. Conclusions

The results of [7–12, 14, 16] prove that DMABN in polar solution exists as a set of various conformers differing in their solvate shells. These forms have their own frequencies of pure electronic transitions ν_{00} and this means that such a solution may be treated as a typical spectrally inhomogeneous system. The character of inhomogeneity can be defined as conformationally configurational. The broadening value registered is anomalously high and spectral shifts of luminescence band with a change of excitation can reach 8000 cm^{-1} .

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