Emission Anisotropy of *p*-Cyano-N,N-Dialkylanilines in Poly(vinyl alcohol) Film

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The emission anisotropy spectra, $r,(\lambda)$ of *p*-cyano-dimethylaniline (CDMA) and *p*-cyano-diethylaniline (CDEA) in PVA films are temperature dependent. At 296 K a characteristic dependence of $r,(\lambda)$ on the absorption (A), short emission (SE) and long emission (LE) band, responsible for the total emission of fluorescence and phosphorescence is observed. On temperature enhancement to 355 K and next to 380 K the phosphorescence is eliminated. In the case studied the emission anisotropy is positive for the fluorescence bands SE and LE and it attains approximately 0.2, confirming thus that the transition moments' directions are in these bands parallel.

Key words: p-Cyano-N,N-Dialkylanilines; Emission Anisotropy; Transition Moments.

1. Introduction

It is known that in polar solvents *p*-cyano-dimethylaniline (CDMA) and *p*-cyano-diethylaniline (CDEA) exhibit two fluorescence bands: short wavelength emission (SE) and long wavelength emission (LE) [1, 2]. According to the hypothesis of Lippert et al. [1] this additional LE band CT (charge transfer) is caused by solvent – induced state reversal, where the polar solvent lowers the more polar ^1L_a state below the less polar ^1L_b state. However, the SE band has been ascribed by those authors to fluorescence from a less polar ^1L_b state. This hypothesis was supported by the measurements of emission anisotropy spectra of CDMA in ethanol at 90 K.

Recently Rettig and Lutze [3] performed also measurements of emission anisotropy of CDMA in ethanol at low temperatures (153 K and 173 K). They found, similarly to [2, and 4 – 6] , that the close to zero value of r of CDMA at the blue edge of the SE band at 330 nm evidences that the emissive state is polarized perpendicularly to the absorbing ^1L_a state. This means that the transition moment is located along the short molecular axis and it derives from the ^1L_b state.

However, the studies of Grabowski and coworkers [7] , being the basis for assuming the hypothesis of the TICT state (twisted intramolecular charge transfer), have shown that the emission anisotropy r measured in viscous glycerol solution at 297 K is positive in the both bands SE and LE. This leads to the conclusion that the SE and LE fluorescences are parallel polarized and the transition moments are located along the long axis of CDMA.

Emission anisotropy spectra are usually measured in glassy (rigid) solutions at temperatures low enough to eliminate depolarization of the fluorescence by Brownian rotations. At temperatures below 273 K, besides fluorescence there appears usually phosphorescence as found also for CDMA embedded in glassy solutions (for example ethylalcohol glass, EPA glass) [8]. To prevent phosphorescence, different rigid polymer matrices are used and the spectroscopic measurements are carried out at room temperature. However, in [9] the important experimental fact has been missed that in the case of CDMA in polyvinyl alcohol (PVA) films apart from fluorescence also phosphorescence is present at room temperature. This phosphorescence band strongly overlaps with the LE band [5,10]. Moreover, in the PVA polymeric matrix microscopic defects, appearing as empty spaces, can be found. In such empty spaces part of the CDMA molecules could twist to the TICT state due to rotational relaxation of the -N$(CH_3)_2$ group.

In view of the different behaviour of the emission anisotropy in SE and LE bands reported by different authors, emission anisotropy spectra of CDMA and CDEA will herein be reexamined. The experimental techniques and PVA preparation have been reported

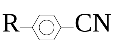	R=N(C_2H_5)$_2$	R=N(CH_3)$_2$
	CDEA	CDMA

Fig. 1. Structural formula of *p*-Cyano-N,N-dialkyl-anilines and their abbreviation.

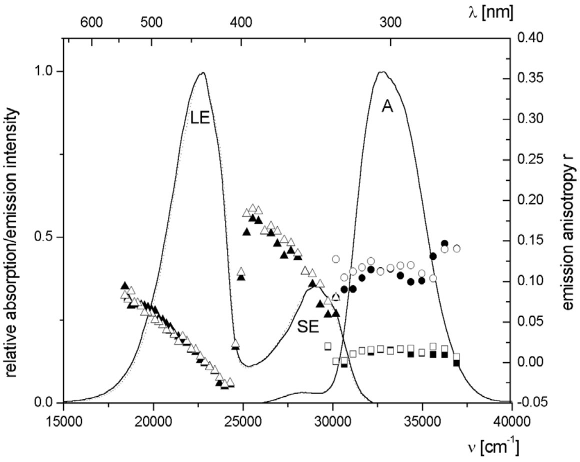

Fig 2. Absorption (A), short- and long wavelength emission spectra (SE, LE) of CDEA in PVA film measured at 296 K before (solid line) and after heating (dashed line). The emission anisotropy spectra before heating (▲) and after heating (△) as well as emission spectra were obtained for λ_{exc} = 305 nm. ●, ○ and ■, □ denote the emission anisotropy data before and after heating, measured at λ_{obs} = 350 nm and λ_{obs} = 450 nm (for various excitation wavelengths), respectively.

previously [11–14]. Figure 1 shows the structural formulas of the compounds studied and the abbreviations used.

2. Results and Discussion

The absorption, emission (SE and LE) and emission anisotropy $r = (I_{\|} - I_{\perp})/(I_{\|} + 2I_{\perp})$, where $I_{\|}$ and $I_{\perp}$ denote the intensity component parallel and perpendicular to the direction of the electric vector of the exciting light, of CDEA and CDMA in PVA at 296 K are presented in Figs. 2 and 3. Figure 2 shows additionally the A, E and emission anisotropy for CDEA in PVA films before and after heating above the glassy transition temperature T_g. The observed agreement between both sets of data is satisfactory. It evidences that the spectra can be studied at room temperature without the necessity of initial heating to T_g = 358 K.

The strange and characteristic course of the experimental r-data at 296 K concerns the total photoluminescence (fluorescence and phosphorescence). To eliminate the phosphorescence, the mentioned spectra were measured at higher temperatures, i. e., 355 K and 380 K (Figs. 4 and 5). As can be seen, due to the phosphorescence quenching, emission anisotropy in the SE and LE band remains at the same level of approximately 0.2 both for CDEA and CDMA, and it does not attain the limiting value of 0.4 predicted by the

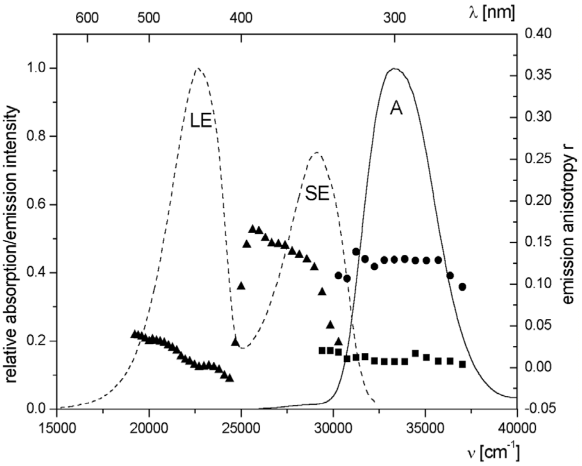

Fig 3. Absorption (A), SE, LE and emission anisotropy spectra of CDMA in PVA film measured at 296 K. The emission and emission anisotropy spectra (▲) were measured for λ_{exc} = 300 nm. ● and ■ denote the emission anisotropies measured at λ_{obs} = 350 nm and λ_{obs} = 450 nm (for various excitation wavelengths), respectively.

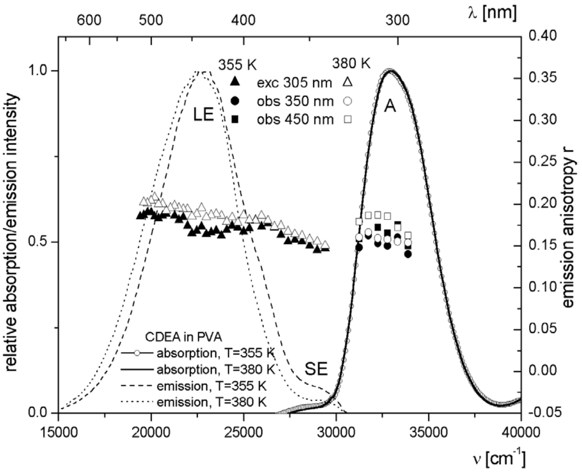

Fig 4. Absorption (A), SE, LE and emission anisotropy spectra of CDEA in PVA film measured at 355 and 380 K. The emission and emission anisotropy spectra (▲, △) were measured for λ_{exc} = 305 nm. ●, ○ and ■, □ denote the emission anisotropies measured at λ_{obs} = 350 nm and λ_{obs} = 450 nm (for various excitation wavelengths), respectively.

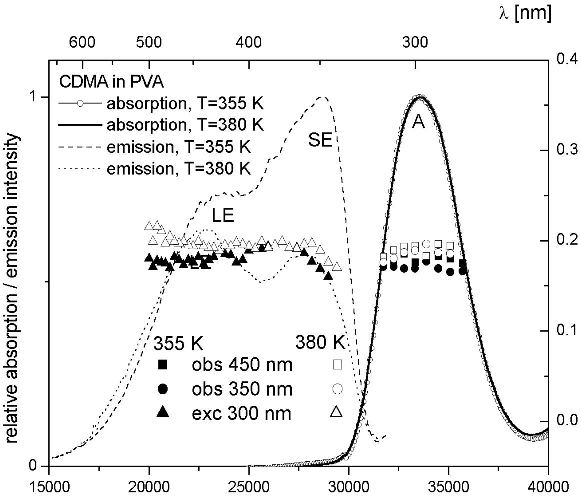

Fig 5. Absorption (A), SE, LE and emission anisotropy spectra of CDMA in PVA film measured at 355 and 380 K. The emission and emission anisotropy spectra (▲, △) were measured for λ_{exc} = 300 nm. ●, ○ and ■, □ denote the emission anisotropies measured at λ_{obs} = 350 nm and λ_{obs} = 450 nm (for various excitation wavelengths), respectively.

theories of Perrin [15] and Jabłoński [16]. Such a low value of *r* evidences the presence of empty spaces in PVA, in which restricted rotations are possible. Positive and close one to another values of *r* in both bands, SE and LE, confirm that the directions of the transition moments are parallel in these bands. The conclusion drawn in [10] is not valid. The different values of *r* in the SE and LE band (0.15 and 0.10, respectively) of CDMA in propylene glycol at 293 K are caused by the significantly different lifetimes: 20 ps and 1.65 ns, respectively [17]. The emission anisotropy decay measurements lead to the conclusion that the initial limiting emission anisotropy, *r(0)*, is the same in the SE and LE bands, and it amounts to 0.28 [17].

It should be mentioned that at the long wavelength side of the absorption band of both molecules (see Figs. 2 – 5) there appears a weak band of much lower absorptivity, similar as observed for the first time by Khalil et al. [18,19] for CDMA and CDEA in different media, like for example ethanol, ethyl acetate, 3-methylpentane and EPA glass. This weak absorption band was ascribed by them to the absorption of a dimer.

The strong decrease of the emission anisotropy over the SE band located around 330 nm observed by different authors, can result from the overlap with the weak absorption band appearing at the long wavelength side of the main absorption band.

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