Influence of the Irradiation Time on the Absorption and Emission Spectra of *p*-Cyano-N,N-Dialkylanilines in Polar Solvents

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Dedicated to Professor Czesław Bojarski on the occasion of his 80th birthday.

The effect of the time of irradiation with the excitation wavelength λ_{exc} on the absorption and emission spectra of *p*-cyano-N,N-dimethylaniline (CDMA), *p*-cyano-N,N-diethylaniline (CDEA) and N,N- dimethylaniline (DMA) in acetonitrile and in *n*-hexane, as well as the effect of high temperature is studied. It is found that after sufficiently long irradiation of CDMA and CDEA in acetonitrile the short wavelength SE band intensity strongly increases compared to that of the long wavelength LE band. This phenomenon is caused by the photolysis of CDMA and CDEA in polar solvents. In each case both the irradiation time and the delivery of suitable thermal energy leads to irreversible processes.

Investigations of the λ_{exc} effect on the location and intensity distribution of emission bands have shown their independence of λ_{exc} ranging from 260 nm to 330 nm in the LE band. However, a pronounced effect of λ_{exc} on the intensity appears in the SE band. In this spectral region DMA molecules formed due to the photolysis of CDMA absorb strongly.

Excitation at λ_{exc} = 340 – 360 nm in the dimeric absorption band leads to a new emission band overlapping the LE band, which indicates the presence of luminescing dimers.

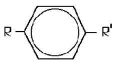
Key words: *p*-Cyano-N,N-Dialkylanilines; Dual Fluorescence; Irradiation Time;
Absorption and Emission Spectra; Photolysis.

1. Introduction

From studies of Lippert et al. [1, 2] it follows that both *p*-cyano-N,N-dimethylaniline (CDMA) and *p*-cyano-N,N-diethylaniline (CDEA) exhibit in polar solvents not only a short wavelength fluorescence band (SE), but also a long wavelength fluorescence band (LE) which is strongly red shifted. They found that after longer irradiation by the exciting light the CDEA molecules decompose due to the splitting of one of the para-substituents [2].

In [3] we have also found that in the case of CDMA in different polar solvents the intensity ratio of both bands, $I^{\mathrm{SE}}_{\mathrm{max}}/I^{\mathrm{LE}}_{\mathrm{max}}$ changes significantly during the measurement after several minutes of irradiation by the selected excitation wavelength. Moreover, we have found that the lifetime observed in the SE band (350 nm) undergoes a significant change. To prevent this we used a cell with flow of the solution studied.

The current paper deals with the influence of the irradiation time on the absorption and fluorescence spectra of CDMA, CDEA and DMA (N,N-dimethylaniline) in the polar solvents acetonitrile, ethyl acetate and ethylene glycol, and for comparison in the unpolar *n*-hexane.



	CDEA	CDMA	DMA
R	$N(C_2H_5)_2$	$N(CH_3)_2$	$N(CH_3)_2$
R’	CN	CN	H

Scheme 1. Chemical structure of *p*-substituted Dialkylanilines

Scheme 1 shows the structural formulas of the compounds studied and the abbreviations used.

2. Experimental

CDMA, CDEA, and DMA were from Aldrich Chemical Company, Inc., Steinheim, Germany and were used without further purification. The experimental techniques for the absorption and photoluminescence measurements as well as the method of preparation of the isotropic PVA films have been reported in [4 – 7]. For spectroscopic measurements at different tempera-

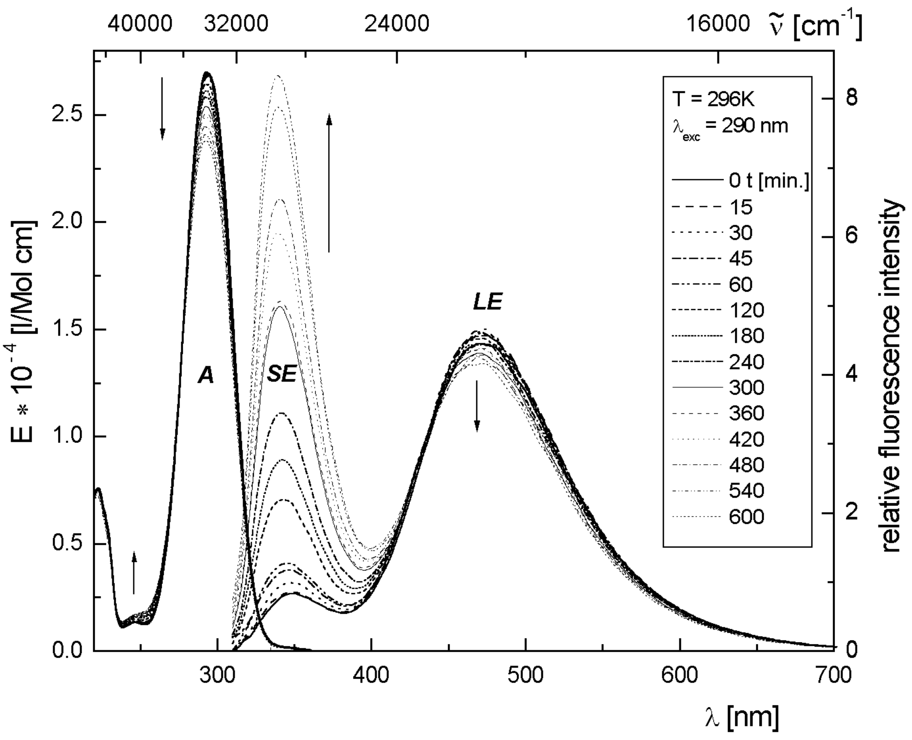


Fig. 1. Absorption (A) and fluorescence (SE and LE) spectra of CDMA in acetonitrile obtained at different irradiation times for the excitation wavelength λ_{exc} = 290 nm.

tures *T*, a high pressure cell described in [8, 9] has been applied.

3. Results and Discussion

It should be noticed that in the long wavelength part of the absorption band around 330 – 360 nm there appears an additional weak band both for CDMA and CDEA in polar solvents. The intensity of this weak band is much smaller than that of the main absorption band which has been found by Khalil et al. [10 – 12] for these compounds in ethanol, ethyl acetate, 3-methylpentane and EPA glass. That weak absorption band was ascribed by them to dimer absorption. We have found this band for the molecules studied not only in polar liquids but also in rigid polymer matrices like PVA [13].

It occurs that during long lasting irradiation of CDMA and CDEA in the polar solvent acetonitrile (permittivity ε = 38.8 and the electric dipole moment μ_g = 3.35 D) with the excitation wavelength λ_{exc} = 290 nm, the SE band intensity increases strongly compared to that of the LE band, whereas the LE band intensity decreases only slightly. This is caused by the significant decrease of the extinction coefficient *E* in the long wavelength part of the absorption band (295 nm) and by a slight increase of *E* around 250 – 265 nm. These facts are shown in Figs. 1 – 3 for CDMA and CDEA in acetonitrile. The isosbestic point for both compounds studied appears at 275 nm, similarly as for CDEA in [2].

It is characteristic for the compounds studied that the intensity of the SE band right after the preparation of the solution and on immediate measurement ($t \approx 0$) is very small compared to that of the LE band (cp. Figs. 1 and 2).

Also the absorption and fluorescence spectra (λ_{exc} = 280 nm) of CDMA and CDEA were measured in the unpolar solvent *n*-hexane. In this case no significant change of the intensity versus irradiation time was found both in the absorption and emission spectra up to 180 minutes, and only one emission band was observed corresponding to the SE band (Fig. 4).

Such a dependence on the time of irradiation is caused by the photolysis of CDMA and CDEA in polar solvents. By the UV radiation one of the para-substituent bonds is broken (probably that of the CN group), and longer irradiation leads to a detectably irreversible process.

A similar phenomenon of breaking the bond is observed as a result of delivering suitable thermal energy.

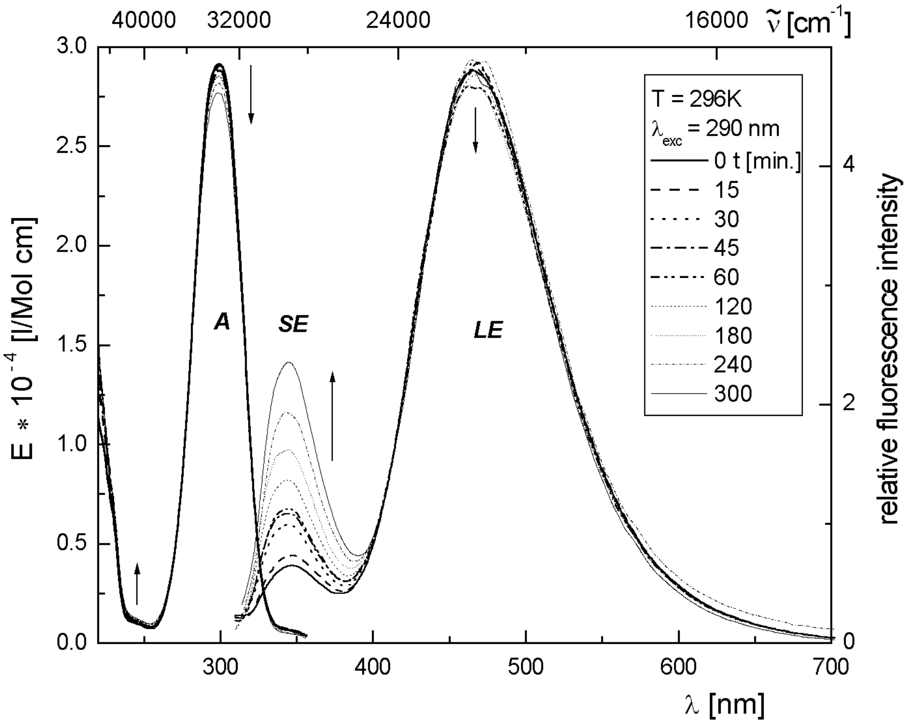


Fig. 2. Absorption (A) and fluorescence (SE and LE) spectra of CDEA in acetonitrile obtained at different irradiation times for the excitation wavelength λ_{exc} = 290 nm.

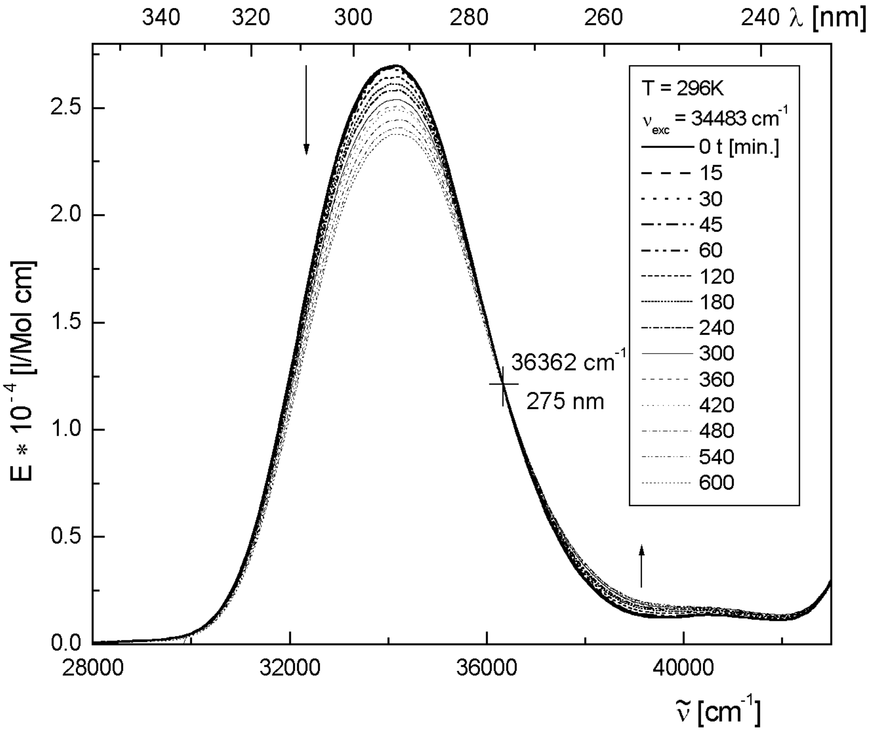


Fig. 3. Absorption spectra of CDMA in acetonitrile obtained at different irradiation times.

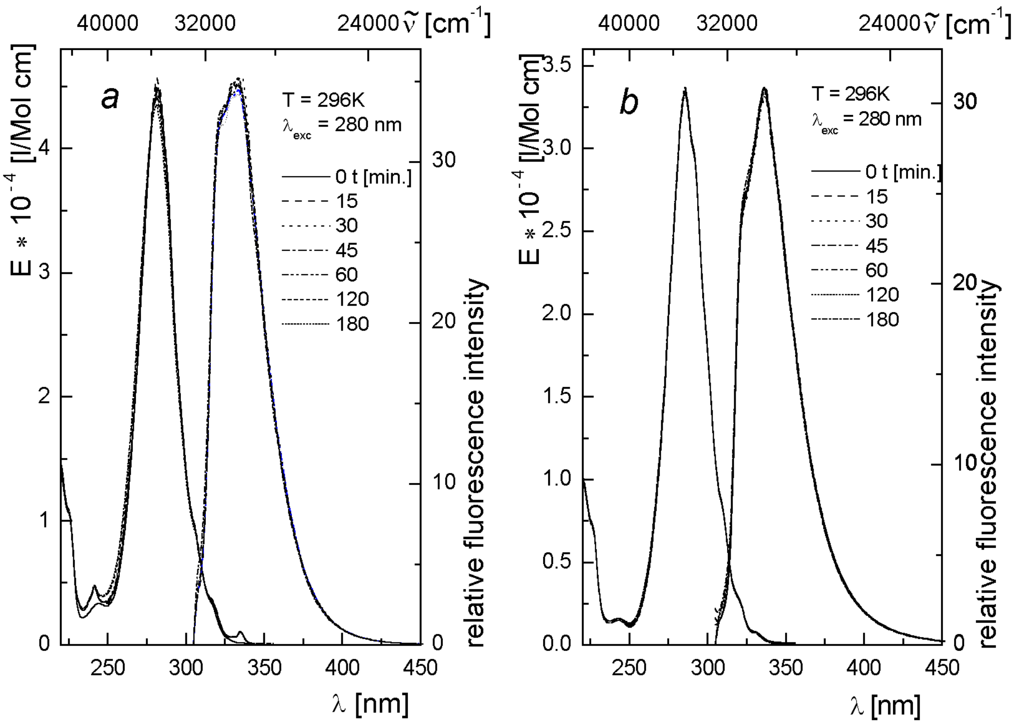


Fig. 4. Absorption and fluorescence spectra of CDMA (Fig. 4a) and CDEA (Fig. 4b) in *n*-hexane obtained at different irradiation times for the excitation wavelength λ_{exc} = 280 nm.

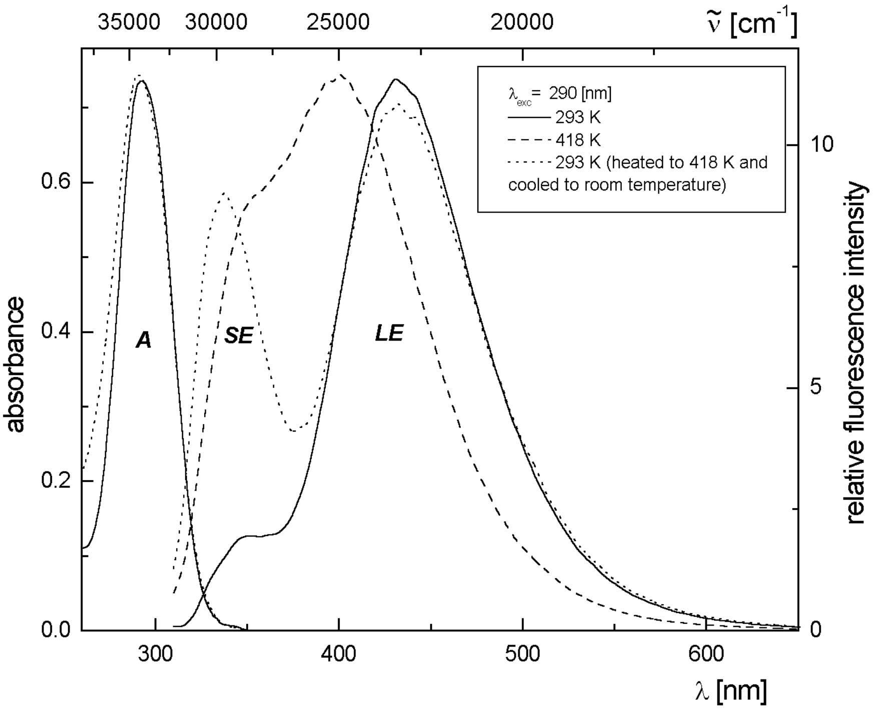


Fig. 5. Absorption (A) and fluorescence (SE and LE) spectra of CDEA in ethyl acetate at 293 and 418 K, and at 293 K after heating to 418 K and cooling to 293 K.

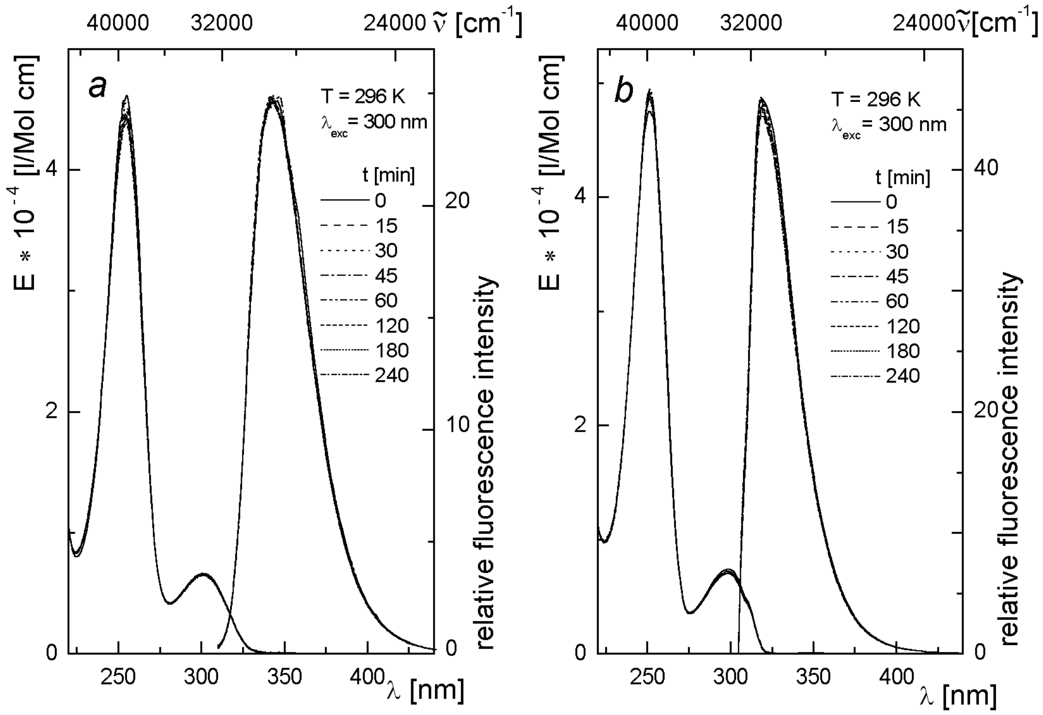


Fig. 6. Absorption and fluorescence spectra of DMA in acetonitrile (Fig. 6a) and *n*-hexane (Fig. 6b) obtained at different irradiation times with the excitation wavelength λ_{exc} = 300 nm.

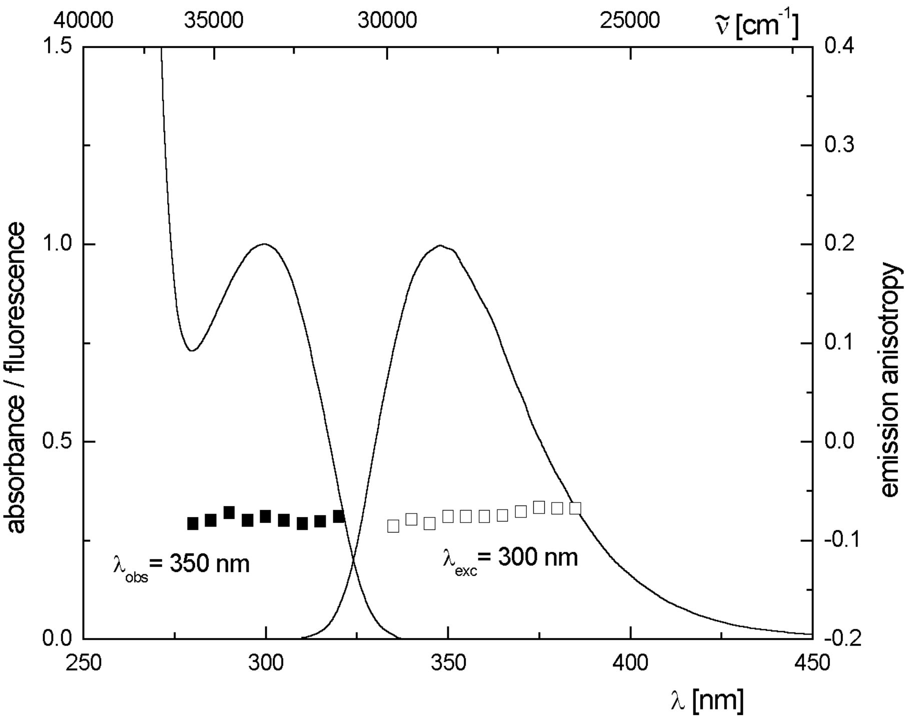


Fig. 7. Absorption, fluorescence and emission anisotropy spectra of DMA in ethylene glycol at 296 K.

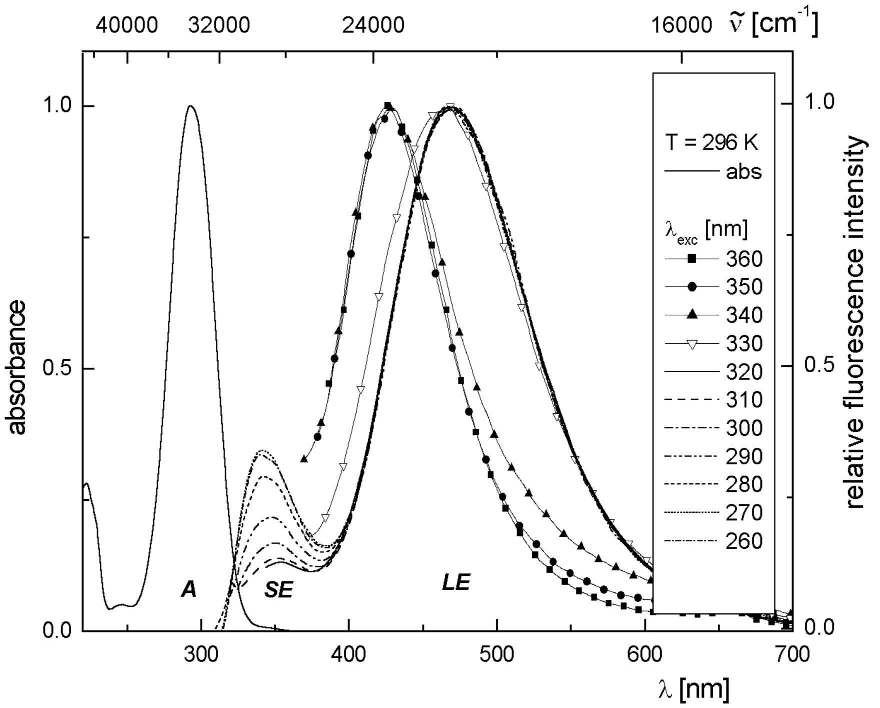


Fig. 8. Absorption (A) and fluorescence (SE and LE) spectra of CDMA in acetonitrile measured at different excitation wavelengths λ_{exc}.

Figure 5 shows the results of absorption as well as SE and LE fluorescence for CDEA in ethyl acetate at 293 K and 418 K. After heating to 418 K and cooling to 293 K, a strong increase of the SE band intensity is observed at room temperature, which results from the formation of a permanent thermoproduct. However, the location of the SE and LE bands at 293 K before and after heating does not change. At 418 K a strong broadening of these bands is observed, accompanied by a significant hypsochromic shift of the LE fluorescence band caused by the decrease of the permittivity ε.

If there is no CN substituent in the CDMA molecule, we obtain a DMA molecule (Scheme 1). Figure 6 shows the measured absorption and fluorescence spectra (λ_{exc} = 300 nm) of DMA in acetonitrile (a) and *n*-hexane (b) for different irradiation times. In this case, for irradiation times up to 240 minutes no significant effect on the observed intensity in the absorption and fluorescence band was found. The fluorescence band in acetonitrile is red shifted by about $\delta\lambda$ = 25 nm compared to the location of the band in *n*-hexane, whereas the long wavelength absorption band in acetonitrile only about $\delta\lambda$ = 3 nm compared to the respective band in *n*-hexane.

The comparison between the fluorescence bands of DMA and CDMA in acetonitrile shows that the DMA fluorescence overlaps totally with the SE band for CDMA, whereas the long wavelength absorption bands of these compounds are only slightly shifted (Figs. 1 and 6a).

The emission anisotropy spectra, *r*, for DMA in ethylene glycol (viscosity η = 16.1 m Pa·s at T = 298 K) exhibit at room temperature negative values – 0.075 (Fig. 7). The strong decrease of the emission anisotropy in the SE band located around 330 – 350 nm observed by different authors for CDMA may be a result of the overlapping with the weak dimeric absorption band appearing at the long wavelength side of the main band [13] or by the overlapping of the absorption and fluorescence bands of DMA (the photoproduct formed due to the photolysis of CDMA) with the absorption and SE fluorescence bands of CDMA.

Quite a different issue is the extremely strong red shifted LE band appearing for CDMA and CDEA only in medium and strongly polar solvents (Figs. 1, 2 and 5). The positive values of the emission anisotropy in the SE and LE bands were a basis of introducing a new class of the excited states: Twisted Intramolecular – Charge – Transfer (TICT) [14]. The TICT state can not be the result of direct absorption, since its geometry is different from that of the ground state. A basic role plays the polar solvent, which stabilizes the highly polar TICT state below the S_1 state [14, 15].

In rigid glasses, which are obtained at low negative temperatures, only SE is observed [14]. However, in a rigid poly(vinyl alcohol) polymer (PVA) at T = 296 K both bands, SE and LE, are observed, which overlap with the phosphorescence band [13]. The difference between rigid PVA films and frozen glasses is that in the first ones microscopic defects are formed, which appear as empty spaces, and this is the reason why part of the CDMA or CDEA molecules may lead to the TICT state due to the rotational relaxation of the -N(CH$_3$)$_2$ or -N(C$_2$H$_5$)$_2$ group. This is confirmed by the positive emission anisotropy of these compounds in the SE and LE bands in PVA films [13].

Moreover, the effect of the excitation wavelength on the fluorescence band location and its intensity distribution for CDMA and CDEA in acetonitrile was studied (Fig. 8). In the absorption region between 260 nm and 330 nm no effect of λ_{exc} in the LE band is observed. However, the excitation wavelength λ_{exc} exhibits a strong effect on the intensity of the SE band. This is caused by the absorption of the DMA molecules formed by the photolysis of CDMA molecules (cp. Fig. 6a). The excitation with $\lambda_{\text{exc}} = 340 \div 360$ nm in the long wavelength part of the main absorption band, i. e., in the dimeric absorption band, leads to the observation of a new emission band overlapping with the LE band (Fig. 8). In this case we deal with the dimers able to emission.

4. Conclusions

The presented investigations allow to draw the following conclusions:

a) The intensity of the SE band for CDMA and CDEA in acetonitrile right after the preparation of the solution and immediate measurement ($t \approx 0$) upon continuous excitation with λ_{exc} = 290 nm is very small compared to the intensity of the LE band. In the course of irradiation the intensity of the SE band strongly increases. This phenomenon is caused by the photolysis of CDMA and CDEA in polar solvents. Due to the absorption of the UV radiation, the bond with one of the para-substituents breaks (probably with the CN group), and longer irradiation leads to a detectable irreversible process.

b) A similar effect on CDMA and CDEA in a polar solvent can be attributed to high temperatures. After heating to 418 K and then cooling to 293 K the intensity of the SE band increases strongly compared to the intensity of the SE band observed at 293 K without heating. This is also a irreversible process.

c) No intensity change has been found in the absorption and SE fluorescence for CDMA and CDEA in the unpolar solvent *n*-hexane as a function of the irradiation time with the excitation wavelength λ_{exc} = 280 nm.

d) In the case of DMA (lacking the CN group compared to CDMA) in acetonitrile and in *n*-hexane, no effect of the irradiation time (λ_{exc} = 300 nm) on the intensity of the absorption and fluorescence band was found. The comparison between the fluorescence of DMA and CDMA in acetonitrile leads to the conclusion that the DMA fluorescence overlaps totally with the SE band of CDMA. The long wavelength absorption bands of these compounds are only slightly shifted.

e) Irradiation with the excitation wavelength λ_{exc} does not exhibit any significant effect on the LE band, which is ascribed to the TICT state. In the absorption region 260 – 330 nm no influence of λ_{exc} on the location and intensity distribution in the LE band was observed. On the contrary, the influence of λ_{exc} on the SE band intensity results from the strong absorption of DMA molecules. The DMA molecules are formed due to the photolysis of CDMA.

f) Excitation with $\lambda_{\text{exc}} = 340 \div 360$ nm in the dimeric absorption band leads to the observation of a new emission band which overlaps with the LE band. This fact evidences the ability of dimers to emit fluorescence.

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