Absorption, Fluorescence and Emission Anisotropy Spectra of 4-Cyano-N,N-dimethylaniline in Different Media and at Different Temperatures

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Z. Naturforsch. **52a**, 409–414 (1997); received March 3, 1997

The effect of temperature on fluorescence and emission anisotropy spectra of 4-cyano-N,N-dimethylaniline (CDMA) was investigated in viscous (glycerol and paraffin oil) and rigid (poly(vinyl alcohol) PVA and poly(vinyl chloride) PVC) media. A strong effect of temperature on the intensity of **a** and **b** emission bands was observed. It was also found that the emission anisotropy, r, does not vary in the longwave emission band **a** at a fixed temperature but decreases in the emission band **b** together with the decreasing wavelength. The latter effect is due to the fact that the transition moment in this band is perpendicular to the long axis of the CDMA molecule. For CDMA in paraffin oil, a normal **b** band with negative emission anisotropy only occurs. In all other media used, the emission anisotropy has lower values, approaching zero, which results from the considerable covering of band **b** with a broad emission band **a**.

1. Introduction

The investigations of Lippert et al. [1–4] concerning light polarization (emission anisotropy) in the absorption and fluorescence bands of p-cyano-N,N-dimethylaniline (CDMA) (synonymous: p-dimethylamino-benzonitrile) and of other similar nitrile compounds have shown that the bands of fluorescence **b** (normal) and fluorescence **a** (anomalous) originate from states having different $^1L_b/^1L_a$ symmetries. In nonpolar solvents, the highly polar state ^1L_a of molecule CDMA is, on the energy scale, situated close to, yet above, the state ^1L_b. In polar solvents, the intermolecular energy interaction of the solvent shell with the polar CDMA molecule shifts the ^1L_a state below the ^1L_b state. Therefore, the respective band of fluorescence **a** lies on the longwave side of the fluorescence band **b**. The higher the polarity of the low viscous solvent, the greater the red shift of band **a** [1, 5, 6].

As shown in [1, 3, 6], the shortwave fluorescence **b** is polarized perpendicularly to the long axis of CDMA, the short axis of which lies in the plane of the aromatic ring. The band of fluorescence **a** is polarized along the long axis and exhibits strong temperature dependence in liquid solvent [5, 7].

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It was demonstrated in addition that the original hypothesis [1, 5, 8] of solvated-induced $^1L_b/^1L_a$ state crossing may be combined with the twisted internal charge transfer (TICT) mechanism [9, 10] to form a consistent intramolecular reaction model [3, 11].

The hypothesis of the TICT states was at first based on the finding that the degree of fluorescence polarization (emission anisotropy) of nitrile compounds similar to CDMA is high and positive in viscous or rigid solutions, irrespective of excitation which is either in the first or the second absorption band [9, 12].

The hypothesis of the TICT mechanism was supported experimentally by measuring the fluorescence of sterically hindered amino compounds [9, 10, 12, 13] and by numerous quantum-mechanical calculations using widely different methods [11, 13–16].

In the measurements of the emission anisotropy, rigid isotropic (polymers or frozen solutions) or highly viscous solutions (e.g. glycerol) are used to prevent rotational motions of solute molecules. It turns out that already at room temperature some of the luminescent compounds embedded in the polymer, such as poly(vinyl alcohol) (PVA) exhibit phosphorescence in addition to fluorescence [17].

In the present paper, the behaviour of the emission anisotropy in the absorption and emission bands of CDMA is investigated in media such as glycerol, paraffin oil, poly(vinyl alcohol) (PVA) and poly(vinyl

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chloride) (PVC) at room and higher temperatures (up to 383 K).

2. Experimental

4-Cyano-N,N-dimethylaniline (CDMA) and glycerol 99.5+% spectrophotometric grade were from Aldrich Chemical Company, Inc., Steinheim, Germany. Paraffin liquid oil for spectroscopy was from Enzymes, England. PVA films were obtained from poly(vinyl alcohol) (100% hydrolyzed, MW 106 000–110 000, Aldrich-Chemie) and PVC films were prepared using poly(vinyl chloride) (BDH Chemicals Ltd., Poole, England; high molecular weight, MW approximately 200 000). Isotropic PVA and PVC films were prepared by the method described in [18, 19]. The CDMA molecules were introduced into PVA and PVC through methanol and tetrahydrofuran, respectively.

Absorption, fluorescence, phosphorescence and emission anisotropy* spectra were measured by methods described in [20, 21].

3. Results and Discussion

3.1. Absorption, Fluorescence and Emission Anisotropy Spectra of CDMA in Glycerol and Paraffin Oil

Figure 2 shows absorption, fluorescence and emission anisotropy spectra of CDMA in glycerol, measured at two different temperatures, 295 and 353 K. It should be noted that the longwave absorption band as well as the symmetrical "normal" band of fluorescence **b** are narrow compared to the "anomalous" band of fluorescence **a**. The emission anisotropy in band **a** markedly exceeds that in band **b** for the maximum dynamic viscosity at 295 K (Table 1). The decreasing of the emission anisotropy in band **b** for the decreasing wavelength means that the transition moment in band **b** is perpendicular to the long axis of CDMA, thus confirming the results reported by Lippert et al. [1–3]. The actual values of the emission anisotropy in band **b** are considerably lower, since the broad **a** band with

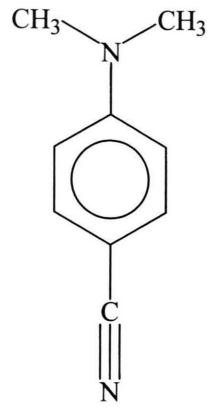

Fig. 1. Structural formula of 4-cyano-N,N-dimethylaniline (synonymous: 4-dimethylaminobenzonitrile) (CDMA).

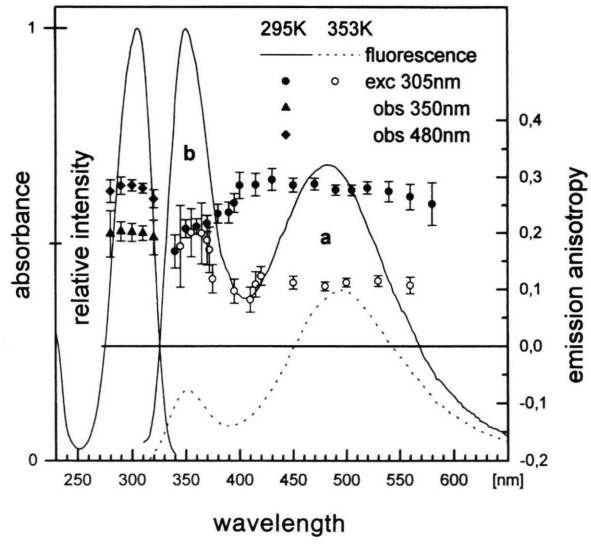

Fig. 2. Absorption, fluorescence and emission anisotropy spectra of CDMA in glycerol at 295 K and 353 K.

high positive emission anisotropy almost completely covers band **b**. Raising the temperature to 353 K results in a strong decrease in the emission anisotropy in band **a** due to an almost 25-fold decrease in the viscosity of the solvent (Table 1). In this case, an essential role is played by the rotational depolarization of fluorescence. The fact that in the fluorescence band **b** the emission anisotropy at 353 K does not markedly differ from that at 295 K can be accounted for by different mean lifetimes of states ^1L_a and ^1L_b. Such a behaviour of the emission anisotropy in both bands is confirmed

* The emission anisotropy is defined by: $r = \frac{I_{\parallel} - I_{\perp}}{I}$, where $I = I_{\parallel} + 2\,I_{\perp}$ is the total fluorescence intensity and $I_{\parallel}$ and $I_{\perp}$ are components parallel and perpendicular, respectively, to the direction of the electric vector of the exciting light.

Table 1.

Liquids name	Dipole moment μ [10^{-30} Cm]*	Dynamic Viscosity [22] [mPa · s]**		Electric permittivity [23]	
		T(K)	η	T(K)	ε
Glycerol	8.90	298	934	298	42.50
		323	152	323	35.53
		348	39.8	348	31.38
		373	14.8	373	27.88
Paraffin oil		293	165 [24]		
		298	134 [25]		

* The conversion factor for the dipole moment: $\frac{[\mu]_{SI}}{\text{Cm}} = 3.33564 \times 10^{-30} \frac{[\mu]_{cgs}}{\text{D}}$, where D is the symbol for debye and $1\,\text{D} = 10^{-18}$ esu cm.

** $1\,\text{cP} = 10^{-3} \frac{\text{kg}}{\text{ms}} = 10^{-3}$ Pa · s.

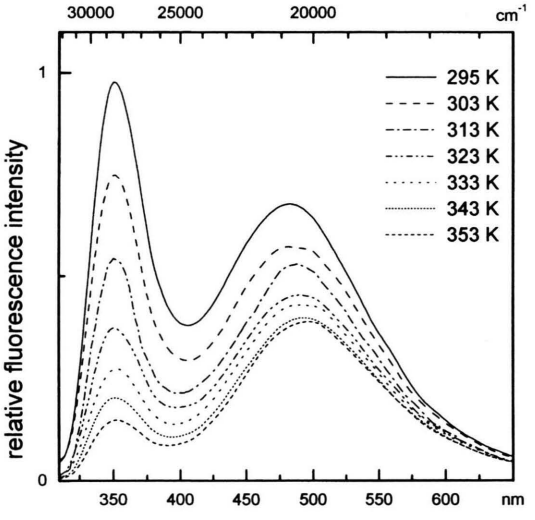

Fig. 3. Fluorescence spectra of CDMA in glycerol at different temperatures (295 ÷ 353 K).

by the measurements of mean lifetimes, $\tau_A = 4.54$ ns and $\tau_B = 10.9$ ps [10].

In Perrin's equation [26, 27] for rotational depolarization of fluorescence,

$$\frac{r_0}{r} = 1 + \chi, \tag{1}$$

an important role is played by the dimensionless constant

$$\chi = \frac{kT}{V\eta}\tau = \frac{\tau}{\tau_D}, \tag{2}$$

where τ_D is the rotational relaxation time, V is the volume of the luminescent molecule embracing the solvent shell, η is the dynamic viscosity of the solvent, r_0 is the fundamental emission anisotropy.

Depending on the value of χ, i.e. on the relationship between the mean lifetime, τ, of the luminescent molecule and the rotational relaxation time, τ_D, either high emission anisotropy ($r \to r_0$ for $\chi \ll 1$) or complete depolarization ($r \to 0$ for $\chi \to \infty$) can be observed. If $\chi = 1$ ($\tau \approx \tau_D$) one obtains $r = r_0/2$.

In band **a**, the emission anisotropy at 353 K decreased about twofold compared with that at 295 K, i.e. the rotational relaxation time, τ_D, is in this case comparable to the mean lifetime τ_A of CDMA in state ^1L_a (or TICT).

Raising the temperature to 353 K results in a strong decrease in the intensity of band **b**, which at 295 K markedly exceeds the intensity of band **a** (Figure 3). In the temperature range examined, the viscosity of glycerol strongly decreases, although not enough for the rotational relaxation time and dielectric relaxation time of the solvent to be by two or three orders of magnitude lower than the mean lifetime of the CDMA molecule in state ^1L_a.

On the other hand, the CDMA molecule placed in paraffin oil exhibits only the normal band of fluorescence **b**, corresponding to the nonpolar solvent (Fig. 4 and Table 1). The emission anisotropy observed at 295 K is clearly negative (Figure 5). The raising of temperature to 353 K causes a decrease in the viscosity of paraffin oil and, hence, results in stronger rotational depolarization of fluorescence. In this case, in accordance with the definition of the emission anisotropy, $r = -(I_\perp - I_\parallel)/I$, attenuation of the perpendicular component, $I_\perp$, occurs and the emission anisotropy approaches zero (see Figure 5).

Mention should be made that the anomalous behaviour of the emission anisotropy observed in bands **a** and **b** of CDMA in propylene glycol [17] can be accounted for, similarly as for the glycerol solution, by different lifetimes of this molecule in states ^1L_a and ^1L_b.

3.2. Absorption, Fluorescence and Emission Anisotropy Spectra of CDMA in PVA and PVC Films

As already demonstrated in [17], CDMA in PVA film at room temperature exhibits both fluorescence

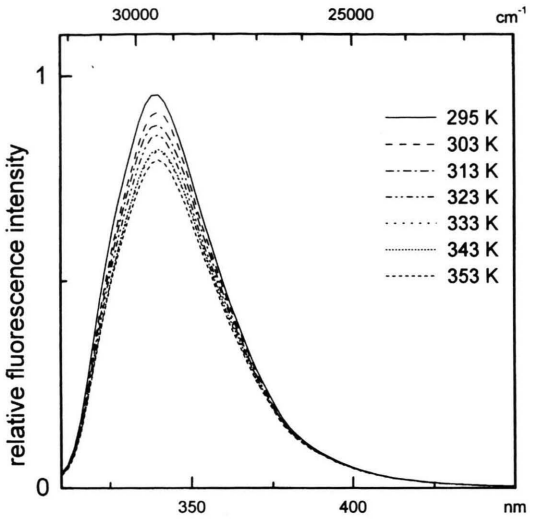

Fig. 4. Fluorescence spectra of CDMA in paraffin oil at different temperatures (295 ÷ 353 K).

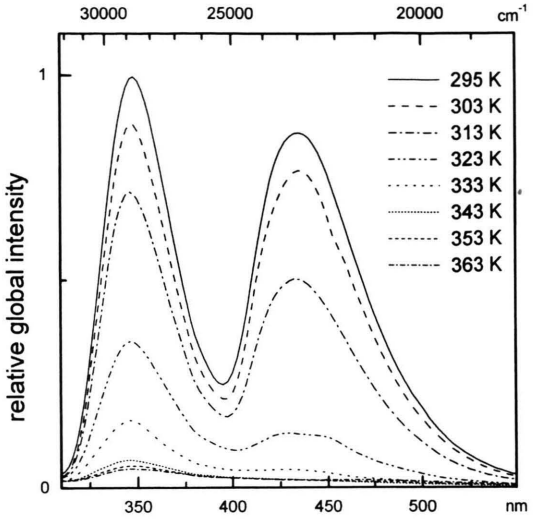

Fig. 6. Global emission spectra (fluorescence + phosphorescence) of CDMA in PVA film at different temperatures (295 ÷ 363 K).

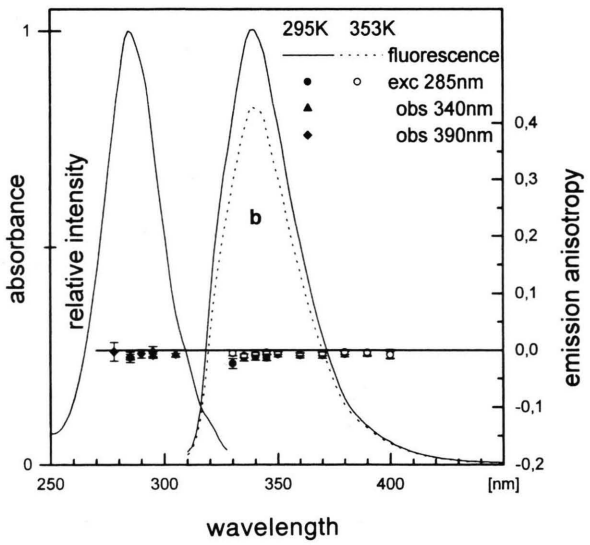

Fig. 5. Absorption, fluorescence and emission anisotropy spectra of CDMA in paraffin oil at 295 K and 353 K.

and phosphorescence. To eliminate the phosphorescence, the behaviour of the emission anisotropy should be examined at elevated temperatures. Figure 6 shows the spectra of the global emission **a** and **b** of the CDMA molecule in PVA film at different temperatures. As seen in Fig. 7, the phosphorescence band lying within band **a** vanishes completely above 343 K. Similarly as in the glycerol solution, a greater broadening of band **a** compared to band **b** can be observed. Elevation of temperature results in a still greater broadening. Above 353 K, the emission anisotropy of the pure fluorescence increased rapidly and did not change within band **a** (Fig. 8), whereas when passing to band **b**, the fluorescence decreased markedly, similarly as for CDMA in glycerol.

Shortwave emission **b** is observed for the same CDMA molecule in the PVC polymer, with a distinct, weakly pronounced band **a** (Figure 9). In this case, no phosphorescence was observed at room temperature. The temperature increase was accompanied by a distinct decrease in the intensity of band **b**, this, however, being somewhat slower than for CDMA in PVA film. Despite the weakly pronounced band **a** (in the longwave part of band **b**), marked emission anisotropy can be observed in the region above 400 nm, whereas within band **b** the anisotropy decreases distinctly with decreasing wavelength (Figure 10).

As seen when comparing the emission spectra for CDMA in PVA and PVC (Figs. 6 and 9), band **a** in PVA is distinctly developed whereas in PVC it its hardly outlined in the longwave part of band **b**. At 353 K (when no phosphorescence occurs for CDMA in PVA), the intensity of band **b** in PVC film is slightly

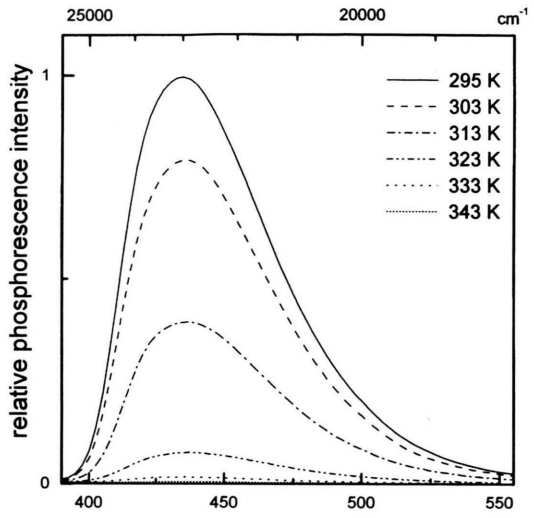

Fig. 7. Phosphorescence spectra of CDMA in PVA film at different temperatures (295 ÷ 343 K).

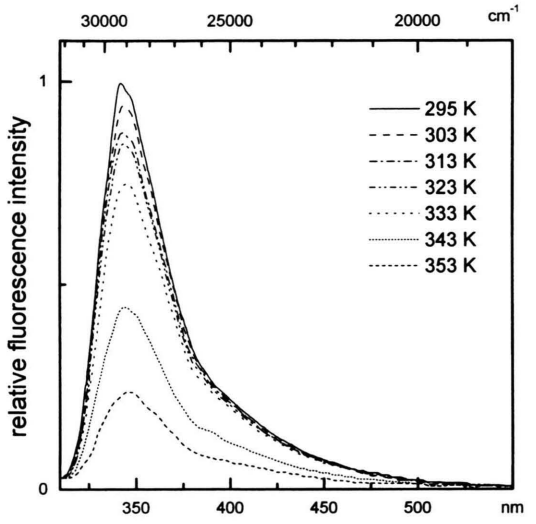

Fig. 9. Fluorescence spectra of CDMA in PVC film at different temperatures (295 ÷ 353 K).

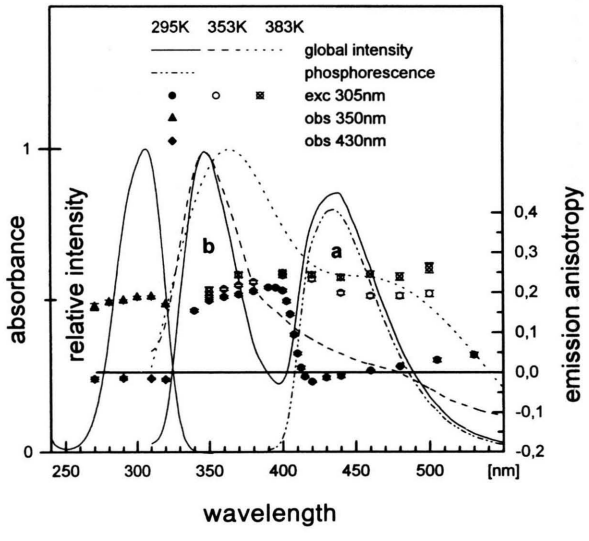

Fig. 8. Absorption, emission and emission anisotropy spectra of CDMA in PVA film at 295 K, 353 K and 383 K.

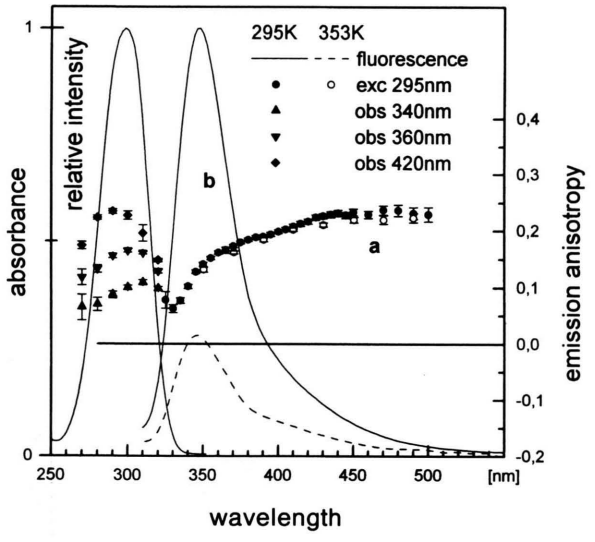

Fig. 10. Absorption, fluorescence and emission anisotropy spectra of CDMA in PVC film at 295 K and 353 K.

higher than that in PVA film. In this case, the polarity of the matrix does not play any significant role since the medium is not liquid. It can only be assumed that the TICT state can only be created as the result of the microscopic defects formed in the PVA and PVC matrices.

Acknowledgement

The authors wish to thank Mr M. Górzyński for his participation in the measurements. This work was supported by grand no. 2P03B 159 12 from the Committee for Scientific Research (Warsaw).

[1] E. Lippert, W. Lüder, F. Moll, W. Nägele, H. Boos, H. Prigge, and J. Seibold-Blankenstein, Angew. Chem. **73,** 695 (1961).
[2] E. Lippert, in: Organic Mol. Photophys., Vol. 2 Ed. by J. B. Birks, Wiley and Sons, Inc. London 1975, p. 1.
[3] W. Rettig, G. Wermuth, and E. Lippert, Ber. Bunsenges. Physik. Chem. **83,** 692 (1979).
[4] G. Wermuth, Z. Naturforsch. **38a,** 368 (1983).
[5] E. Lippert, W. Lüder, and H. Boos, in: Advances in Molecular Spectroscopy, Ed. by A. Mangini, Pergamon Press, Oxford 1962, p. 443.
[6] E. Lippert, in: Luminescence of Organic and Inorganic Materials, Eds. H. P. Kallmann and G. M. Spruch, Wiley and Sons, Inc. New York 1962, p. 271.
[7] A. Kawski and G. Piszczek, Z. Naturforsch. **52a,** 289 (1997).
[8] E. Lippert and W. Rettig, J. Mol. Structure **45,** 373 (1978).
[9] K. Rotkiewicz, K. H. Grellmann, and Z. R. Grabowski, Chem. Phys. Lett. **19,** 315 (1973).
[10] K. Rotkiewicz, Z. R. Grabowski, A. Krówczyński, and W. Kühnle, J. Luminescence **12/13,** 877 (1976).
[11] W. Rettig and V. Bonačić-Koutecky, Chem. Phys. Lett. **62,** 115 (1979).
[12] Z. R. Grabowski, K. Rotkiewicz, W. Rubaszewska, and E. Kirkor-Kamińska, Acta Phys. Polon. **A54,** 767 (1978).
[13] Z. R. Grabowski, K. Rotkiewicz, A. Siemiarczuk, D. J. Cowley, and W. Baumann, Nov. J. Chim. **3,** 443 (1979).
[14] D. J. Cowley and A. H. Peoples, J. Chem. Soc. Chem. Commun. 352 (1977).
[15] J. Lipiński, H. Chojnacki, Z. R. Grabowski, and K. Rotkiewicz, Chem. Phys. Lett. **70,** 449 (1980).
[16] V. Bonačić-Koutecky and J. Michl, J. Amer. Chem. Soc. **107,** 1765 (1985).
[17] A. Kawski, G. Piszczek, and B. Kukliński, Z. Naturforsch **50a,** 949 (1995).
[18] A. Kawski and Z. Gryczyński, Z. Naturforsch. **41a,** 1195 (1986).
[19] A. Kawski, Developments in Polarized Fluorescence Spectroscopy of Ordered Systems, in: Optical Spectroscopy in Chemistry and Biology – Progress and Trends (D. Fassler, ed.) VEB Deutscher Verlag der Wissenschaften, Berlin 1989.
[20] A. Kawski, G. Piszczek, B. Kukliński, and T. Nowosielski, Z. Naturforsch. **49a,** 824 (1994).
[21] A. Kubicki, Exp. Tech. Phys. **37,** 329 (1989).
[22] CRC Handbook of Chemistry and Physics, ed. D. R. Lide, 73RD Edition 1992–1993, CRC Press Boca Raton, **6**-167.
[23] Landolt-Börnstein, Springer-Verlag Berlin 1959, p. 618.
[24] E. Döller und Th. Förster, Z. Phys. Chem. N. F. **34,** 132 (1962).
[25] E. D. Cehelnik, R. B. Cundall, J. R. Lockwood, and T. F. Palmer, J. Chem. Soc. Faraday Trans. **2,** 70, 244 (1974).
[26] F. Perrin, Ann. Phys. Paris **12,** 159 (1929).
[27] Th. Förster, Fluoreszenz Organischer Verbindungen, Vandenhoeck und Ruprecht, Göttingen 1951.