

Rotation of PRODAN in excited state

VLADIMIR I. TOMIN

Institute of Physics, Pomeranian University, Arciszewskiego 22B, 76-200 Słupsk, Poland;
e-mail: tomin@if.pap.edu.pl

Instant spectra and anisotropy kinetics of PRODAN luminescence in different ranges of spectra has been studied upon excitation by picosecond pulses. Instant spectra of luminescence reveal time dependent Stokes shift having intermolecular nature as its characteristic time correlates with dielectric relaxation time of solvent. The mean Brownian rotation time for the curves obtained shows complex character of spectral dependence with maximum ~ 39 ns near maximum of luminescence intensity and drops down to 15 ns on the edges of the spectrum. An explanation is based on a treatment of intermolecular energy conversion into thermal movement of molecules during relaxation in excited state. Calculations using hydrodynamic model show "stick" boundary conditions for solutes: rotational volumes correspond to solute together with molecules of the first coordinative sphere filled by solvent.

Keywords: PRODAN, luminescence, rotation, excited state, charge transfer states, conformers, relaxation.

1. Introduction

In 1970, it was shown [1–3] that apart from molecular vibrations there is another cause of the substantial broadening of electronic spectra of organic molecules in solution, namely, the fluctuations of the structure of the solvation shell surrounding the molecule. The variations of the local electric field caused by the thermal fluctuations of the shell structure and interaction of this field with a solute dipole lead to a statistical distribution of the frequencies of the electronic transitions and, therefore, to inhomogeneous broadening (IB) of the solute spectrum.

A great deal of interest is concentrated on molecules showing significant change in polarity during electronic transition upon excitation and having the ability to create both the local-excited, and charge transfer states [4–7]. Hence, in polar solutions such luminophors must show a sensitivity to solvatochromic effects that is strong enough and reveal the spectral inhomogeneity due to the environmental influence [4–9]. Indeed, the excited electronic states with internal charge transfer of some molecules show an anomalously strong inhomogeneous broadening of their electronic spectra as was shown for laurdan [10] and *n*-dimethylaminobenzonitrile (DMABN), in polar solvents [11–13]. A large group of spectroscopic unusual features registered upon

excitation on the red edge of absorption band, so-called red edge effects, are directly associated with IB of electronic spectra. It is well known that widely used luminescence probe PRODAN changes its polarity during electronic transition, so that the dipole electric moment grows from $\mu_g \approx 2.3$ D in the ground state up to ~ 6.9 D in the excited configuration [14]. The spectroscopic properties of this solute and their peculiarities due to IB have not been studied yet.

Here, we present results of the study into anisotropy kinetics of PRODAN luminescence upon excitation by picosecond pulses. The obtained data show unusual dependence of Brownian rotation time on a wave number of emission registration.

2. Experimental

Absorption and emission were registered by 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 $\lambda = 403$ nm. The registration of luminescence was carried out by time-correlated single photon counting method using PicoQuant techniques. Anisotropy was monitored by a single beam method (L-format) [15]. PRODAN (Lancaster Synthesis, 99.9%) was used without further purification at the concentrations of 10^{-6} – 10^{-3} M.

3. Results and discussion

The luminescence spectra of PRODAN in glycerol at various excitation wavelengths and the spectra of emission excitation are presented in Fig. 1 for a solution at a temperature of 260 K. It is seen that transfer to excitation at the red edge of absorption band is followed by a strong shift of emission band to the long wavelengths about 700 cm^{-1} . There is a considerable simultaneous narrowing of the spectra: a drop is observed from 3600 cm^{-1} at $\nu_{\text{ex}} = 27000\text{ cm}^{-1}$ down to 2360 cm^{-1} at $\nu_{\text{ex}} = 21740\text{ cm}^{-1}$. An increase of the temperature is accompanied by a proper drop of bathochromic shift, which becomes weakly noticeable already $T = 330$ K.

The spectra of Fig. 1 are different for various wavelength of excitation and, hence, this fact directly points to the existence of different molecular forms of PRODAN in solution (more details and discussion of this conclusion is in our paper [16]). Such peculiarities have been well studied for phthalimide derivatives and some other dyes [2, 4–7].

We have studied the kinetics of luminescence instant spectra, time shifts of emission maxima being presented in Fig. 2 (see also [16]). As one can see, maximal emission band shift takes place for 1 ns, then a slower shift is seen during 15 ns, and total spectral shift reaches 2800 cm^{-1} . One may ascribe the observed relaxational shift to intermolecular processes as dielectric relaxation time of glycerol at room temperature is about 1 ns.

The time dependence of emission anisotropy is shown in Fig. 3 for different wave numbers of registration: 22220 and 17860 cm^{-1} . As can be seen from the figure, at

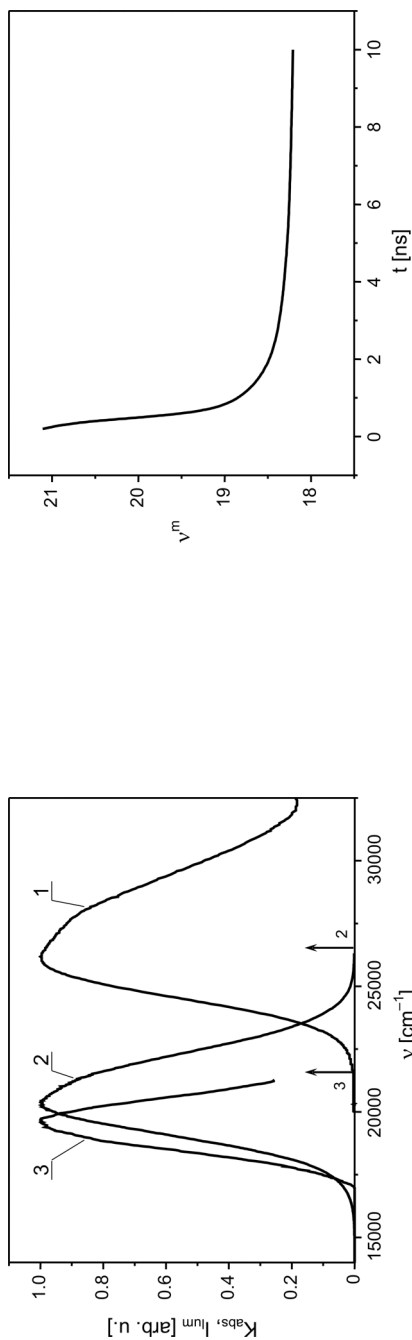


Fig. 1. Spectra of absorption (1) and luminescence (2, 3) of PRODAN in glycerol obtained by exciting the luminophor at ν_{ex} : 27030 cm^{-1} (2) and 21740 cm^{-1} (3), $T = 260 \text{ K}$.

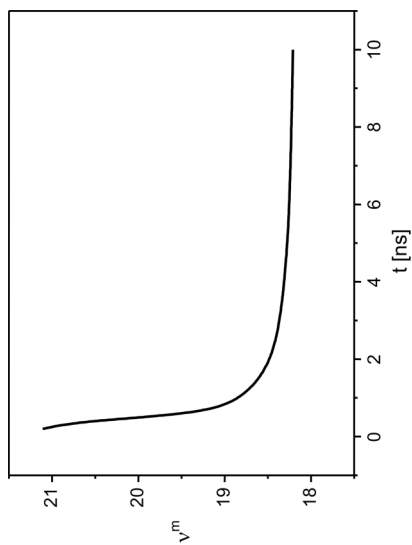


Fig. 2. The time dependences of luminescence instant spectra maximum upon excitation by 65 ps pulses at a wavelength of 403 nm.

Table. Deconvolution of PRODAN in glycerol emission anisotropy pulses on the sum of three exponents; A_i and τ_i are the amplitude and time of the i -th component, $\lambda_{\text{ex}} = 403 \text{ nm}$ (24813 cm^{-1}), $C = 10^{-4} \text{ M}$.

Wavelength/wave number of registration [nm/cm^{-1}]	Amplitude and time component							
	A_1	τ_1 [ns]	A_2	τ_2 [ns]	A_3	τ_3 [ns]	Mean square deviation χ^2	$\langle \tau_p \rangle$ [ns]
450/22220	0.381	4.954	-0.175	10.486	-0.347	2.65	1.201	14.22
520/19230	0.088	1.234	-0.427	17.708	0.724	33.23	1.138	40.09
560/17860	0.419	8.364	0.213	0.694	0.174	24.882	1.485	17.18

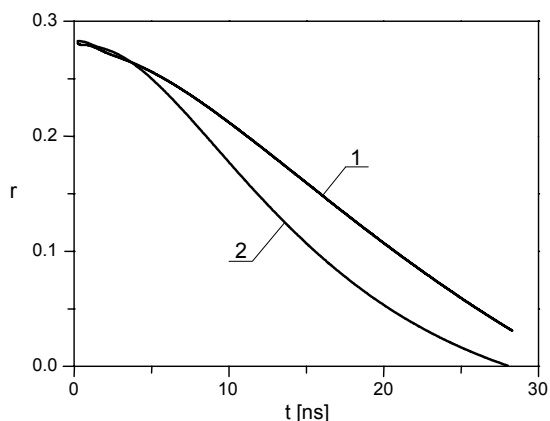


Fig. 3. The pulses of anisotropy for wave numbers: 17860 cm^{-1} (1) and 22220 cm^{-1} (2).

time instant $t = 0$ the anisotropy r_0 is equal to ~ 0.28 , then it drops quite slowly within the time interval $\sim 25\text{--}30$ ns, practically down to 0. The magnitude of r_0 does not practically depend on the wavelength of registration, however, this is not the case for times $t \neq 0$, where anisotropy $r(t)$ decreases faster at higher wave numbers of registration.

The results of anisotropy kinetics decomposition of PRODAN in glycerol are presented for different wave numbers of registration in the Table. As is seen in all the cases, the emission kinetics can be presented as the sum of three exponents with characteristic times from 1.2 up to 33 ns. The longest component ~ 33 ns is for the wave number 19230 cm^{-1} , the shortest one, 10.48 ns is at 22220 cm^{-1} , and finally, near the wave number 17860 cm^{-1} we have a component of about ~ 25 ns. There is no negative component only at the wave number near 17860 cm^{-1} . Characteristically, the mean Brownian rotation time $\langle \tau_B \rangle$, representing a drop of anisotropy as a whole, has maximum ~ 40 ns at 19230 cm^{-1} and shorter values of 14 and 17 ns at higher wave numbers 22220 and 17860 cm^{-1} , respectively.

The data obtained confirm that there is a rotation of the solute, in addition to the Brownian diffusion. The magnitude of this rotation during the relaxation time depends on the amount of realized free energy. Such an effect can be regarded as wavelength dependent rotation and was observed earlier in polar solutions of phthalimides and some other dyes in membranes [4, 17]. More likely, the phenomenon of wavelength dependent rotation is a universal one and should be taken into account when considering the properties of different liquid systems which include solutes with IB spectra. The intermolecular relaxation is accompanied by the release of the free energy excess (about 2800 cm^{-1} for our case), which is converted into heat and warms up a solvate. Naturally, the latter process causes a decrease of viscosity and a wavelength dependent rotation of the solute observed. An increase of the temperature takes place during the relaxation process and, consequently, local T must be higher at long-wave

part of the spectrum to which emission band moves. Therefore, the effect of wavelength dependent rotation is most pronounced when the recording is carried out at the long-wave part of the emission spectrum and the excitation frequency is localized near the absorption maximum. Such a case takes place in emission registration near 17860 cm^{-1} .

In turn, low value of the Brownian rotation time 14 ns, for the wave number 22220 cm^{-1} may be explained by the presence of essential depolarization force just after the pulse of excitation was switched on. The rotation thus stimulated, which represents some kind of “initial shock” in solute solvates, was first observed in some solutions of phthalimide derivatives [4] and 1 phenylnaphthylamine [17]. Some time later, after such an “initial shock” solvates lost “memory” about the latter and relaxed to the equilibrium state in agreement with the above described mechanism of free energy conversion into heat.

When using a hydrodynamic model of Stokes–Einstein–Debye, the Brownian rotation times $\langle\tau_B\rangle$ over the interval 20–25 ns correspond to rotating volumes with radii 1.1–1.3 nm, which are visibly larger than PRODAN dimensions 0.4–0.5 nm [14]. Taking into account the dimensions of glycerol molecules $\sim 0.3\text{ nm}$ [18], one can conclude that a rotating volume of our solvate is restricted by the sizes of the first coordinative sphere. Such a result is not strange as dipole moment of PRODAN in excited state is quite high $\sim 7\text{ D}$ [14] and is able to attract considerable number of glycerol molecules possessing, in turn, a pretty large dipole moment $\sim 3.7\text{ D}$.

Thus, the data presented show an acceleration of PRODAN rotation together with its shell during the process of intermolecular relaxation in solution. This result is not in line with an earlier hypothesis about the slowing of solute rotation as a consequence of “fur” forming and dielectric friction of a solute with electronic shell of its environment [19].

Acknowledgements – The author is grateful to the Pomeranian University in Słupsk, Poland, for partial financing of the work (the project BW6/8/1239/04), prof. P. Kwiek (University of Gdańsk, Poland) and mgr K. Hubisz for experimental.

References

- [1] GALLEY W.C., PURKEY R.M., *Role of heterogeneity of the solvation site in electronic spectra in solution*, Proceedings of the National Academy of Sciences USA **67**(3), 1970, pp. 1116–21.
- [2] RUBINOV A.N., TOMIN V.I., *Bathochromic luminescence in solutions of organic dyes at low temperatures*, Optics and Spectroscopy **29**(6), 1970, pp. 578–80 (original: Optika i Spektroskopiya, **29**(6), 1970, pp. 1082–6).
- [3] WEBER G., SHINITSKY M., *Failure of energy transfer between identical aromatic molecules on excitation at the long wave edge of the absorption spectrum*, Proceedings of the National Academy of Sciences USA **65**(4), 1970, pp. 823–30.
- [4] NEMKOVICH N.A., RUBINOV A.N., TOMIN V.I., *Topics in Fluorescence Spectroscopy*, [Ed.] J.R. Lakowicz, Vol. 2, Principles, Plenum Press, New York 1991, p. 367.
- [5] RUBINOV A.N., TOMIN V.I., BUSHUK B.A., *Kinetic spectroscopy of orientational states of solvated dye molecules in polar solutions*, Journal of Luminescence **26**(4), 1982, pp. 377–91.

- [6] MAZURENKO Yu.T., *Broadening of the electronic spectra of complex molecules in a polar medium*, Optics and Spectroscopy **33**(1), 1972, pp. 22–6 (original: Optika i Spektroskopiya **33**(1), 1972, pp. 42–50).
- [7] DEMCHENKO A.P., *The red-edge effects: 30 years of exploration*, Journal of Luminescence **17**(1), 2002, pp. 19–50.
- [8] LIPPERT E., RETTIG W., BONACIC-KOUTECKY V., HEISEL F., MIEHE J.A., *Photophysics of internal twisting*, [In] *Advances in Chemical Physics*, [Ed.] I. Prigogine, S.A. Rice, Vol. 68, Wiley 1987, p. 1.
- [9] GRABOWSKI Z.R., ROTKIEWICZ K., RETTIG W., *Structural changes accompanying intramolecular electron transfer: focus on twisted intramolecular charge-transfer states and structures*, Chemical Reviews **103**(10), 2003, pp. 3899–4032.
- [10] TOMIN V.I., BROZIS M., HELDT J., *The red-edge effects in laurdan solutions*, Zeitschrift für Naturforschung **58a**, 2003, pp. 109–17.
- [11] TOMIN V.I., HUBISZ K., *Anomalous inhomogeneous broadening of the electronic spectra of N,N-dimethylaminobenzonitrile in solutions*, Journal of Applied Spectroscopy **70**(5), 2003, pp. 804–6.
- [12] TOMIN V.I., HUBISZ K., MUDRYK Z., *Anomalous inhomogeneous broadening of electronic spectra of molecules with internal charge transfer*, Zeitschrift für Naturforschung **58a**, 2003, pp. 529–36.
- [13] TOMIN V., HUBISZ K., *Band broadening in the electronic spectra of 4-dimethylaminobenzonitrile in polar solvents*, Russian Journal of Physical Chemistry **78**(7), 2004, p. 1114.
- [14] KAWSKI A., KUKLIŃSKI B., BOJARSKI P., *Thermochromic shifts of absorption and fluorescence spectra and excited state dipole moment of PRODAN*, Zeitschrift für Naturforschung **55a**, 2000, pp. 550–4.
- [15] LAKOWICZ J., *Principles of Fluorescent Spectroscopy*, Springer 2006.
- [16] TOMIN V., HUBISZ K., *Inhomogeneous spectral broadening and the decay kinetics of the luminescence spectra of prodan*, Optics and Spectroscopy **101**(1), 2006, pp. 98–104.
- [17] NEMKOVICH N.A., RUBINOV A., *Spectral inhomogeneity and wavelength-dependent rotation of probe molecules in membranes*, Journal of Fluorescence **5**(3), 1995, pp. 285–94.
- [18] ZEVANDROV N.D., NIKOLAEV V.P., *Doklady Academy Nauk USSR* **113**(5), 1957, p. 1025.
- [19] LAKOWICZ J.R., *Time-dependent rotational rates of excited fluorophores: A linkage between fluorescence depolarization and solvent relaxation*, Biophysical Chemistry **19**(1), 1984, pp. 13–23.

Received January 30, 2006