Rotational Depolarization of Fluorescence of Prolate Molecules *

A. Kawski, Z. Kojro, P. Bojarski, and J. Lichacz

Luminescence Research Group, Institute of Experimental Physics, University of Gdańsk, Gdańsk, Poland

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The theory of rotational depolarization of fluorescence, taking into account the inertial effect, has been verified experimentally for two angular velocity autocorrelation functions obtained for both the approximate and the exact Langevin equation. To this end, the emission anisotropy was investigated as a function of viscosity for PPO, POPOP, and α-NOPON in liquid *n*-paraffins (from $n=5$ to $n=11$) at 304.5 K. For these three luminescent molecules with mean lifetimes of about 1 ns, and the viscosities ranging from 0.22 to 0.9 cP, no essential difference was found between the experiment and the theory for the angular velocity autocorrelation functions employed.

1. Introduction

Experimental investigations [1–5], carried out for numerous prolate luminescent molecules whose emission transition moment coincides with the long axis of the molecule, revealed marked deviations from the linear Perrin relation describing the dependence of the relative emission anisotropy [1], r/r_0, on the magnitude of T/η (where r_0 denotes the limiting value of the emission anisotropy in rigid or highly viscous solution at low concentration, η is the viscosity, and T the absolute temperature) in particular at low viscosities. It was found that this discrepancy resulted from the neglect of inertial effects in the theories of rotational depolarization of fluorescence, although as far back as in 1930 this effect was taken into account by Uhlenbeck and Ornstein [6] in Einstein's theory on the Brownian motions. Since then, only Gajsenok et al. [7] and Alicki et al. [8] undertook an effort to eliminate the inconsistency between the experimental results and the rotational depolarization theory by taking into account the inertial moments of the luminescent molecules. In the theory of Gajsenok et al. [7], a less precise equation of the rotational diffusion, which was obtained by Steele [9] and, before, by Kubo [10], was employed, whereas in the theory of Alicki et al. [8] the non-Markovian generalized diffusion equation was used. The effect of the moment of inertia on the rotational fluorescence depolarization was demonstrated in both theories [11]. Later, the theory [8] was generalized by Alicki and Alicka [12] to embrace also asymmetric molecules, the directions of the emission and absorption transition moments of which were not coincident, making in general nonzero angles with the principal axes of the inertia tensor.

In the generalized diffusion equation for the rotational motions of molecules, employed by Alicki et al. [8, 12] in the rotational fluorescence depolarization theory, the angular velocity autocorrelation function was introduced in relation to the molecular axis (in the case of a prolate molecule, with respect to axes 1 and 2 perpendicular to the longitudinal axis 3). The diffusion equation employed therein describes the "memory" effect (convolution integral) related with the moment of inertia. A molecule with a moment of inertia behaves during a consecutive collision in the solution as if it remembered the preceding collision and, hence, its motion is in part determined.

A year after the report [8] had appeared, a paper by Morita [13] was published in which the Brownian rotational motions of non-spherical molecules were investigated in terms of the theory of dielectric relaxation. In order to calculate the angular velocity autocorrelation function for a symmetrical molecule (axis 3 being the symmetry axis) Morita employed a more general Langevin equation differing from that used by Alicki et al. [8] by the terms of the order of $(\omega_k \omega_l)$ (see [12]).

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[1] The emission anisotropy is defined by $r=(J_{\parallel}-J_{\perp})/J$, where $J=J_{\parallel}+2J_{\perp}$ is the total fluorescence intensity and $J_{\parallel}$ and $J_{\perp}$ are the components parallel and perpendicular, respectively, to the direction of the electric vector of the exciting light.

Reprint requests to Prof. Dr. A. Kawski, Universytet Gdański, Instytut Fizyki Doświadczalnej, ul. Wita Stwosza 57, 80-952 Gdańsk, Poland.

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When the angular velocity autocorrelation function obtained by Morita [13] and derived from the generalized Langevin equation is taken into account in the theory [8], the equation for the rotational fluorescence depolarization assumes the form

$$\frac{\tau^2}{\frac{r_0}{r}-1} = \frac{I}{6kT} + \frac{V\eta\tau}{kT} + \frac{1}{6}\,\frac{\tau^2 b(1-b)^2}{1+\frac{6V\eta\tau}{I}\,\frac{1+b}{b}}, \qquad (1)$$

where $b = I_3/I$ is the ratio of the moments of inertia ($I_1 = I_2 = I$), V the effective volume of the luminescent molecule, and τ its mean lifetime in the excited state. Formula (1) differs from that obtained by Alicki et al. [8, 14] in the third term on the right-hand side of the equation[2]. For $\eta \to 0$, (1) reduces to

$$\frac{\tau^2}{\frac{r_0}{r}-1} \to \frac{I}{6kT} + \frac{1}{6}\tau^2 b(1-b)^2. \qquad (2)$$

As the viscosity grows, the third term in (1) becomes negligible. It is therefore essential that the validity of formula (1) be verified for extremely low viscosities, which constitutes the goal of the present paper.

2. Experimental

The compounds examined were: 2,5-diphenyloxazole (PPO), 2,2′-p-phenylene-bis(5-phenyloxazole) (POPOP), and p-bis[2-(5-α-naphthyloxazolyl)]-benzene (α-NOPON) (Figure 1). All fluorescent substances were purified prior to the measurements by multiple recrystallization, and the purity was checked by TLC. The solvents were spectroscopically pure. The temperature of the samples, 304.5 K, was kept constant with an ultrathermostat within ±0.2 K.

The absorption and fluorescence spectra of the compounds were measured as previously described [15]. The measurements were fully automatic and controlled by a microcomputer.

The fluorescence anisotropy was measured by the single photon counting technique, with an accuracy of 0.001, using the apparatus described in [16, 17]. The limiting emission anisotropy, r_0, of the compounds was measured in polyvinyl alcohol (PVA) films.

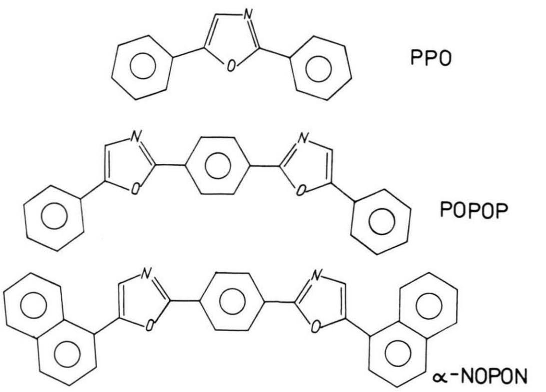

Fig. 1. Structural formulae of PPO, POPOP and α-NOPON.

Table 1. Calculated (Eq. (3)) and measured viscosities η of n-paraffins at 304.5 K.

Solvent	η (in cP)*	
	from (3)	experimental values
n-pentane	0.22	–
n-hexane	0.29	–
n-heptane	0.38	0.37 ± 0.02
n-octane	0.47	0.46 ± 0.02
n-nonane	0.58	0.58 ± 0.02
n-decane	0.72	0.77 ± 0.03
n-undecane	0.86	0.89 ± 0.03

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

The mean fluorescence decay times, τ, were measured by the correlated single photon counting technique [18, 19]. An airfilled spark lamp was used as a source of pulses with a frequency of about 20 kHz. The parameters of the excitation pulses were: pulse rise time 900 ps, half pulse duration 1.75 ns. The STOP and START pulses were measured with Philips XP 2020 and RCA 931 A photomultipliers, respectively. POPOP in ethanol, with a fluorescence decay time of 1.37 ns [20], was used as a standard. All measurements were carried out by the technique described in [21]. The decay times were analyzed by the difference method of deconvolution [22]. The mean emission anisotropies and mean fluorescence decay times were measured at the same excitation wavelengths: 315 nm for PPO and 337 nm for POPOP and α-NOPON.

The viscosities of the saturated hydrocarbons C_nH_{2n+2} were calculated with a formula given by Adamczewski and Calderwood [23], valid for $n = 1$ to

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[2] For $I_3 \approx 0$ and $I_1 = I_2 = I \neq 0$ (the case of a long molecule), $b = 0$, and for $I_1 = I_2 = I_3$ (a sphere), $b = 1$. Hence, the third term in (1) disappears and the equation obtained by Alicki et al. [8] holds true.

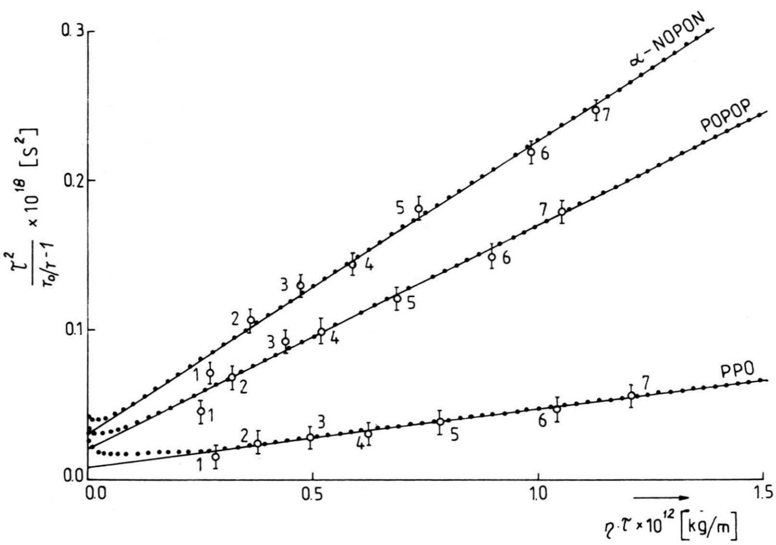

Fig. 2. Dependence of $\tau^2/(r/r_0-1)$ on $\eta\tau$ for PPO, POPOP and α-NOPON in different paraffins at 304.5 K:
(1) n-pentane, (5) n-nonane,
(2) n-hexane, (6) n-decane,
(3) n-heptane, (7) n-undecane.
(4) n-octane,
Dots: According to (1).

$n=64$, at temperatures ranging from 88 to 573 K:

$$\eta=2.54\cdot 10^{-4}\exp(-0.0235\,n)\exp[(416\sqrt{n}-230)/T]. \tag{3}$$

Independently, the viscosities of n-heptane, n-octane, n-nonane, n-decane, and n-undecane were measured at $T=304.5$ K with a Höppler viscosimeter. Some difficulties occurred in the viscosity determination of n-pentane and n-hexane due to their low viscosity and low boiling point. Table 1 summarizes the calculated and measured viscosities. The agreement is good.

3. Results and Discussion

According to (1), the knowledge of b, describing the ratio of the minimal moment of inertia ($I_{\min}\equiv I_3$) with respect to the long axis of the molecule to the maximum moment of inertia ($I=I^{\mathrm{av}}_{\max}$) perpendicular to this axis, is indispensable. Table 2 summarizes the relevant moments of inertia of the molecules investigated, calculated from the lengths and directions of the interatomic bonds. As seen in Fig. 1, the symmetry of the molecules considered is not perfect, $I^{\mathrm{av}}_{\max}/I_{\min}$ being large (Table 2). These molecules can therefore serve as good models for the verification of (1). The mean lifetimes at 304.5 K in n-heptane amount to 1.34, 1.18, and 1.26 ns for PPO, POPOP and α-NOPON, respectively. They do not differ essentially from the lifetimes in the remaining solvents. For example, for POPOP and α-NOPON in n-decane, lifetimes of 1.20 and 1.28 ns were measured. The values of the limiting anisotropy, r_0, determined in a rigid medium (PVA) amount to 0.324, 0.339 and 0.315 ns for PPO, POPOP and α-NOPON, respectively, differing significantly from the value of the fundamental anisotropy, $r_0=0.4$.

Table 2. Calculated mean moments of inertia I (in 10^{-44} kg m^2) of free molecules.

Compound	$I^{\perp}_{\max}$	$I^{\parallel}_{\max}$	$I^{\mathrm{av}}_{\max}=\frac{I^{\parallel}_{\max}+I^{\perp}_{\max}}{2}$	$I_{\min}$	$b=\frac{I_{\min}}{I^{\mathrm{av}}_{\max}}$
PPO	4.3	4.6	4.45	0.39	0.088
POPOP	18.3	19.7	19.0	1.43	0.075
α-NOPON	32.6	34.1	33.35	1.73	0.052

$I^{\parallel}_{\max}$: Moment of inertia with respect to the axis in the plane of the molecule perpendicular to the long axis of the molecule and passing through the centre of mass.
$I^{\perp}_{\max}$: Moment of inertia with respect to the axis perpendicular to the plane of the molecule and passing through its centre of mass.
$I_{\min}$: Moment of inertia with respect to the long axis of the molecule.

Terms of (1) obtained with measured values for PPO, POPOP and α-NOPON in the solvents listed in Table 1 are presented in Figure 2. Straight lines, plotted through the experimental points by the least squares method, correspond to (1) with the third term on the right-hand side omitted. This way the effective moments of inertia, I_{eff}, and effective volumes, V_{eff}, listed in Table 3 were determined. For I_{eff}, V_{eff}, and b thus obtained, the theoretical dependences described by (1) are presented by dots in Figure 2. As readily seen, for all luminescent molecules investigated, both

Table 3. Effective moments of inertia, I_{eff}, and effective volumes, V_{eff}, of luminescent molecules.

Compound	I_{eff} (10^{-40} kg m^2)		V_{eff} (10^{-30} m^3)
	Eq. (1) *	Eq. (2)	
PPO	1.5	1.5	171
POPOP	5.1	5.1	624
α-NOPON	7.5	7.5	823

* with disregard of the third term.

equations (with and without the third term in (1)) correspond very well to the experimental points in a broad range of $\eta\tau$. However, the theoretical curves (dotted lines obtained for (1) embracing the third term) differ only in the range of the lowest $\eta\tau$ values, i.e., when $\eta \to 0$ or τ becomes very small. This range of $\eta\tau$ is, however, beyond the experimental capabilities of verification for PPO, POPOP, and α-NOPON molecules. It is worth pointing out that the differences for the initial lowest values of $\eta\tau$ between the curves (solid and dotted curves) for α-NOPON is smaller than those observed with PPO and POPOP, i.e., for the lowest ratio, b, of the moments of inertia. This is in agreement with (1) since for $b \to 0$, the formula of Alicki et al. [8] is obtained.

It can moreover be anticipated that for symmetrical molecules with I_3 comparable to I_1 and I_2, the parameter b will markedly stronger affect the run of the curve determined by (1). However, for linear prolate luminescent molecules with lifetimes of about 1 ns, and the viscosities ranging from 0.22 to 1 cP, the third term in (1) is of minor importance. In order to have access to the range of $\eta\tau$ in which the difference between the curves considered occurs it is advisable to examine also luminescent molecules with mean lifetimes of the order of 100 ps and less, with parameter $b \neq 0$. This slight deviation of curves at low values of $\eta\tau$ does not affect the magnitude of the determined moments of inertia. The values of I_{eff} obtained with (2), valid for $\eta \to 0$, do not differ from those calculated according to (1) with disregard of the third term. For comparison, the values obtained from the approximation (2) have also been given in Table 3.

The values of I_{eff} and V_{eff} determined in various solvents differ obviously from those calculated for free molecules, which results from the solvation effect. The values of I_{eff} obtained for POPOP and α-NOPON in cyclohexane from the measurements of the mean lifetime and emission anisotropy of fluorescence quenched by nitrobenzene amount to 1.8×10^{-40} kg m^2 and 4.52×10^{-40} kg m^2 [19], respectively, and are about half the values given in Table 3 and obtained by the method of different solvents.

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