The Inertial Effect in Rotational Fluorescence Depolarization

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The influence of the moment of inertia on the rotational fluorescence depolarization is discussed. Based on experimental results obtained for five luminescent compounds: 2,5-diphenyloxazole (PPO), 2,2'-p-phenylene-bis(5-phenyloxazole) (POPOP), p-bis[2-(5-a-naphthyloxazolyl)]-benzene (a-NOPON), 4-dimethylamino-o-methylsulphonyl-trans-styrene (3 a) in n-parafines at low viscosity (from $0.22 \times 10^{-3} \text{ Pa \cdot s}$ to $0.993 \times 10^{-3} \text{ Pa \cdot s}$) and diphenylenestilbene (DPS) in different solvents, a semi-empirical equation is proposed, yielding moments of inertia that are only two to five times higher than those estimated from the molecular geometry.

It was recently discovered that the initial evolution of the emission anisotropy $r(t)$ and its stationary value $r$ depend on the moment of inertia of a luminescent molecule (LM) [1–3]. This effect is related to the change of the state of the rotating LM being conditioned not only by the acting instantaneous moment of a force but also by the LM's moment of inertia.

In the generalized diffusion equation for the rotational motions of molecules employed by Alicki et al. [2, 3] in the rotational fluorescence depolarization theory, the introduced angular velocity autocorrelation function describes the "memory" effect (convolution integral) related with the moment of inertia.

For a prolate LM the change of the emission anisotropy, $r$, with time is given by [2]

$$\frac{dr(t)}{dt} = -6 \int_0^t G(s) r(t-s) \, ds \tag{1}$$

where $G(s) = \langle \omega(0) \omega(s) \rangle$ is the autocorrelation function of the angular velocity with respect to the molecular axis (in the case of a prolate LM, with respect to the axes 1 and 2 perpendicular to the longitudinal axis 3).

Applying the Laplace transform to both sides of (1) at a point $1/\tau$ one obtains

$$\frac{\tau}{r} - 1 = 6 \int_0^\infty G(t) \exp \left\{ -t/\tau \right\} \, dt = 6 \mathcal{L} \left[ \langle \omega(0) \omega(t) \rangle \right], \tag{2}$$

where $\mathcal{L}$ denotes the Laplace transform, $\tau$ the mean lifetime in the excited state, $r$ the limiting emission anisotropy, $V$ the effective volume of the LM, $I$ the moment of inertia with respect to axes perpendicular to the long axis of the LM and $T$ its mean lifetime in the excited state.

For $\tau \to 0$, the second term on the right-hand side of (4) disappears and the well-known Perrin equation is obtained.

The $I$ values previously determined from (4) for a great number of prolate LMs in nonpolar and polar solvents with different viscosities are about three orders of magnitude greater than those calculated from its geometry [2, 4–7]. One of the reasons may be the specific interaction of the LM with the different solvent molecules. Investigations on the long living (about 1.25 ns) molecules 2,5-diphenyloxazole (PPO), 2,2'-p-phenylene-bis(5-phenyloxazole) (POPOP) and p-bis[2-(5-a-naphthyloxazolyl)]-benzene (a-NOPON) in n-parafins, in the absence of strong solute-solvent interactions, at low viscosities (from $0.22 \times 10^{-3} \text{ Pa \cdot s}$ to $0.993 \times 10^{-3} \text{ Pa \cdot s}$) have not given better results...
Table 1. Moments of inertia, $I$, and effective volumes, $V$, of luminescent molecules.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$r_0$</th>
<th>$\tau_0$</th>
<th>$V/kT$ [10$^{-9}$ 1/pa]</th>
<th>$V$ [10$^{-30}$ m$^3$]</th>
<th>$I$ [10$^{-44}$ kg $\cdot$ m$^2$]</th>
<th>$I_{\text{geom}}$</th>
<th>$I$/$I_{\text{geom}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPO</td>
<td>0.324</td>
<td>3</td>
<td>44</td>
<td>186</td>
<td>9</td>
<td>4.5</td>
<td>2</td>
</tr>
<tr>
<td>POPOP</td>
<td>0.339</td>
<td>8</td>
<td>164</td>
<td>690</td>
<td>58</td>
<td>19</td>
<td>3</td>
</tr>
<tr>
<td>$\alpha$-NOPON</td>
<td>0.315</td>
<td>14</td>
<td>219</td>
<td>919</td>
<td>174</td>
<td>33.4</td>
<td>5.2</td>
</tr>
<tr>
<td>3a</td>
<td>0.375</td>
<td>5.4</td>
<td>42.4</td>
<td>171</td>
<td>22.6</td>
<td>5.0</td>
<td>4.5</td>
</tr>
<tr>
<td>DPS</td>
<td>0.3030</td>
<td>5</td>
<td>222</td>
<td>898</td>
<td>17</td>
<td>18.7</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Fig. 1. Dependence of $\tau \left( \frac{r}{r_0} - 1 \right)$ on $\eta$ for PPO ($\bullet$), POPOP ($\square$) and $\alpha$-NOPON ($\triangle$) at 304.5 K and for 3a ($\circ$) at 293 K in different n-paraffins (pentane, hexane, heptane, octane, nonane, decane and undecane). The viscosities of the solvents are given in [8, 9]. The correlation coefficients for PPO, POPOP, $\alpha$-NOPON and 3a are 0.990, 0.993, 0.996 and 0.996, respectively.

Fig. 2. Dependence of $\tau \left( \frac{r}{r_0} - 1 \right)$ on $\eta$ for DPS (●) at 293 K in different solvents (benzene, cyclohexane, n-propanol, n-butanol, n-heptanol, triethyl-ester-glycerol, 1,2-propanediol, cyclohexanol). The viscosities of the solvents are given in [15]. The correlation coefficient is 0.999.

[8]. For short living LMs (about 30 ps), such as trans-stilbene and 4-dimethylamino-ω-methylsulphonyltrans-styrene (3a), the $I$ values determined from (4) differ from those calculated for the free LM by only two orders of magnitude [6, 9].

In the present paper we report an investigation of the linear dependence of $\tau \left( \frac{r}{r_0} - 1 \right)$ on $\eta$ given by (4) for extremely low viscosities, and we are searching for the zero viscosity intercept $\tau_0$. The experimental results obtained for PPO, POPOP, $\alpha$-NOPON and 3a in n-paraffins are shown in Figure 1. The data fit fairly well the straight line corresponding to (4). It can also be seen that the intercept $\tau_0$ is not zero. Thus, both viscous and inertial effects contribute to the orientational relaxation of the LM in these solvents. Table 1 summarizes the values of $V/kT$ and $\tau_0$ for the investigated LMs (see Figure 1).

A similar linear dependence of the reorientation times, determined from depolarized light scattering, on viscosities was found by Bauer et al. [10, 11]. The intercept $\tau_0$ was found to be similar to the reorientation time $\tau_{FR}$ of a classical free rotor [12–14],

$$
\tau_0 \equiv \tau_{FR} = \frac{2\pi}{9} \left( \frac{I}{kT} \right)^{1/2}.
$$
The moments of inertia, $I$, for PPO, POPOP, $\alpha$-NPOPO and $\alpha$, determined from (5) for the intercept $TQ$ values obtained (see Table 1), differ only from two to five times from those calculated for free molecules. Equation (4) can be replaced with the semi-empirical equation
\[
\frac{\tau}{r_0} = \frac{V}{kT}\eta + \frac{2\pi}{9}\left(\frac{I}{kT}\right)^{1/2}.
\]

Equation (6) was verified also for the previously studied nonpolar molecule of diphenylstilbene (DPS) in solvents of different polarity and viscosity [15]. The linear dependence of $\tau\left(\frac{r_0}{r} - 1\right)$ on $\eta$ was obtained in a large viscosity range (from $0.65 \times 10^{-3}$ Pa·s to $68 \times 10^{-3}$ Pa·s) (Fig. 2) and the value of $I$ obtained was 1.1 times as large as that calculated, $I_{\text{geom}}$ (see Table 1).

The autocorrelation functions employed by Alicki et al. [2, 3], Morita [16] and Lynden-Bell and Steele [17] are only approximations of the true autocorrelation function. Lynden-Bell and Steele [17] have assumed that a molecule can temporarily be located in a certain limited cavity in the liquid, performing harmonic librations (restricted rotations) with different frequencies. They obtained a function similar, but not identical, to that of Morita, which for the case when the degree of fluctuations of cavities in the liquid approaches zero, is equal to the autocorrelation function used by Grzywacz and Trumpakaj [18, 19].

The search for a reasonable shape of the angular velocity correlation function is fully justified and should contribute to further explanation of the nature of rotational motions of LMs in liquids.

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