Influence of Inertial Effect on Fluorescence Anisotropy

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Z. Naturforsch. **42 a,** 123–126 (1987); received May 16, 1986

The influence of inertial effects on the fluorescence anisotropy r is discussed.

From recent work on the anisotropy of a prolate fluorescent molecule in a liquid solvent it is known that its estimated experimental moment of inertia is as much as about 3 orders of magnitude greater than that calculated from its geometry.

In this paper, by using a non-exponential form of the memory function $K(t)$ in the generalized relaxation equation for $r(t)$, a satisfactory agreement between measured and calculated moments of inertia is obtained.

Introduction

The influence of the molecular reorientation on the depolarization of the fluorescent light in liquid solutions has been discussed by Perrin [1] and Jabłoński [2].

The time-dependent fluorescence anisotropy $r(t)$ in an isotropic liquid may be expressed as

$$\frac{r(t)}{r(0)} = \tfrac{1}{2}\langle 3\cos^2\theta(t) - 1\rangle , \tag{1}$$

where $\theta(t)$ is the angle between the absorption and emission vectors and the brackets $\langle \ldots \rangle$ denote the ensemble average.

The Jabłoński's theory [3] is very general and yields values of $r(0)$ within the limits

$$-0.2 \le r(0) \le 0.4 .$$

However, for linear rotators having a transition moment parallel to their long axis, Alicki et al. [4] suggested the generalized relaxation equation

$$-\frac{\mathrm{d}r(t)}{\mathrm{d}t} = \int_0^t K(t')\, r(t-t')\, \mathrm{d}t' , \tag{2}$$

in which $K(t)$ is the first memory function [5–8] proportional to the angular velocity autocorrelation function [4]. Assuming an exponential decay of the excited electronic states, $\exp(-t/\tau_F)$ together with a single exponential decay of $K(t)$ appearing from the Langevin equation for angular velocities, they obtained the following expression for the steady-state fluorescence anisotropy r:

$$\frac{r(0)}{r} = 1 + \frac{\tau_F/\tau_R}{1 + A\,\tau_F/\tau_R} \tag{3}$$

with

$$A = I/(6\,k\,T\,\tau_F^2) , \tag{3a}$$

where τ_F is the mean lifetime of fluorescence, τ_R the reorientatioal relaxation time (equal to $V\eta/kT$) and I the largest moment of inertia of the fluorescent molecule.

Equation (2) points to a new aspect of the Brownian orientational depolarization. Nevertheless, (3) and (3 a) are unsatisfactory in so far as the moments of inertia estimated from experimental data [9, 10, 11] with (3) and (3 a) are by about three orders of magnitude greater than those calculated from geometrical molecular parameters [11]. These discrepancies are mainly due to the inadequacy of the applied memory function $K(t)$. We will show that a simple semi-empirical function $K(t)$ [12] leads to a reasonable agreement between theoretical and experimental quantities.

Theoretical Considerations

The right side of (1) defines the angular position autocorrelation function $G(t)$ [13]. On the other hand, $G(t)$ is connected with the first memory function $K(t)$ as follows [5–8]:

$$-\frac{\mathrm{d}G(t)}{\mathrm{d}t} = \int_0^t K(t')\, G(t-t')\, \mathrm{d}t' . \tag{4}$$

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This equation is formally identical with (2). Both functions $r(t)/r(0)$ and $G(t)$ describe the same molecular motion, thus

$$r(t)/r(0) = G(t)\,. \tag{5}$$

If we have the function $G(t)$ or $K(t)$ with a known decay of fluorescence, $\exp(-t/\tau_F)$, we are able to calculate the steady-state fluorescence anisotropy r either from

$$\frac{r}{r(0)} = \frac{1}{\tau_F} \int_0^\infty G(t) \exp(-t/\tau_F)\, dt \tag{6}$$

or (by Laplace transformation of (2)) from

$$\frac{r(0)}{r} = 1 + \tau_F \int_0^\infty K(t) \exp(-t/\tau_F)\, dt\,. \tag{7}$$

The function $G(t)$ can be experimentally determined, for instance, from the depolarized scattered light spectrum by its Fourier transformation. Then $K(t)$ can be calculated directly from (4). Typical experimental shapes of $G(t)$ and $K(t)$ obtained in this way [12] are shown in Figs. 1 and 2, where $K(t)$ is clearly non-exponential.

It is well known from other experiments [8, 7], as well as from molecular dynamics simulations [14, 15] that $K(t)$ possesses always a positive and negative lobe. However, the analytical approaches [4, 16] basing on a Langevin type equation of motion lead to positive values of $K(t)$ only. Thus, the correct value of r can be evaluated basing on an experimental $G(t)$ or $K(t)$. However, experimental data are often incomplete and not always obtainable. Therefore it is useful to fit the experimental function $K(t)$ by an analytical expression. Trumpakaj [12, 17] has suggested the following formula:

$$K(t) = \frac{6kT}{I} \exp\left(-\frac{pkTt^2}{2I}\right) \cdot \cos\left(t\sqrt{\frac{p(2E-qkT)}{I}}\right), \tag{8}$$

which can be proved theoretically with a modified Gaussian Cage Model /GCM/ [12]*.

The GCM is based on the idea that the distribution of the libration frequencies is Gaussian. The parameters p, q and E can be determined experimentally. (For example, in liquid carbon disulphide $p = 22$, $q = 2.82$ and $E = 6.3$ kJ/mol.) According to the interpretation in [12], E is the activation energy for reorientation, p is associated with the number of nearest neighbours and q with the heat capacity.

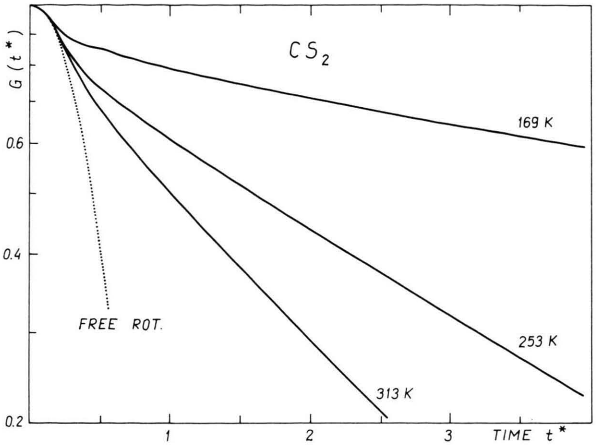

Fig. 1. Some experimental angular position correlation functions $G(t^*)$ obtained from the depolarized light scattered from liquid carbon disulphide [12]. The time scale is in the reduced units $t^* = t\sqrt{kT/I}$.

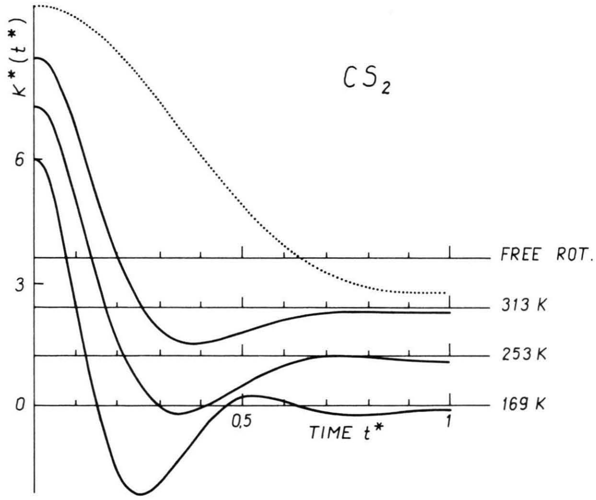

Fig. 2. Some experimental first memory functions $K^*(t^*)$ obtained from $G(t^*)$ as in Fig. 1 by means of (4) (Ref. [12]). $t^* = t\sqrt{kT/I}$; $K^*(t^*) = K(t^*) \cdot I/kT$.

The reorientational relaxation time τ_{REL} may be expressed from its definition and (8) by

$$\tau_{REL} = 1/\int_0^\infty K(t)\, dt = \tau_0 \exp(E/kT - q/2)\,, \tag{9}$$

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* The details of deriving (8) are given in [12].

where

$$\tau_0 = \sqrt{pI/18\pi kT} \tag{9a}$$

is an inertial term with the moment of inertia I of the fluorescent molecule.

Hydrodynamics theories yield the relation $\tau_R = V\eta/kT$ [18–20], but experimental results [19–22] suggest that the relaxation time tends to a constant, $\tau_{0\eta} > 0$, when the shear viscosity η is extrapolated to zero, i. e.

$$\tau_{REL} = \tau_{0\eta} + \tau_R = \tau_{0\eta} + V\eta/kT\,. \tag{9b}$$

Thus, taking into account that right sides of (9) and (9b) should be equal, we have

$$\exp\,(E/kT - q/2) = (\tau_{0\eta} + V\eta/kT)/\tau_0\,. \tag{9c}$$

The relation (9c) links the activation energy E with the viscosity η.

Now the integral in (7) can be expressed analytically by

$$\frac{r(0)}{r} = 1 + \frac{\tau_F}{\tau_{0\eta} + V\eta/kT} \cdot \frac{1}{\sqrt{\pi}} \sum_{i=0}^{\infty} \left(-\frac{6\sqrt{\pi}\,\tau_0}{p\,\tau_F}\right)^i \frac{\Gamma\left(\frac{i+1}{2}\right)}{i!} \cdot \Phi\left(-\frac{i}{2}, \frac{1}{2}; \frac{E}{kT} - \frac{q}{2}\right), \tag{10}$$

where

$$\Phi(\alpha, \gamma; x) = 1 + \frac{\alpha}{1!\,\gamma} \cdot x + \frac{\alpha(\alpha+1)}{2!\,\gamma(\gamma+1)}\,x^2 + \dots$$

and $\Gamma(x)$ is the gamma function.

For $\tau_F \gg \tau_0$ and low values of η, (10) becomes (3) in which, however, the parameter A is replaced by

$$C = \tau_{0\eta}/\tau_F\,. \tag{11}$$

Although $\tau_{0\eta}$ does not appear in any hydrodynamic theory, it is often identified with the free rotator correlation time.

If we identify $\tau_{0\eta}$ with τ_0 (see Table 1) then

$$C = \tau_0/\tau_F = \sqrt{pA/3\pi}\,.$$

Let us remark that in our case C is proportional to $\sqrt{A}$, where A is given by (3a). In consequence instead of $A \propto I$ in (3) we have got $C \propto \sqrt{I}$ in the equivalent equation (10). Thus, the calculated moment of inertia I is now comparable with its experimental value (Table 1) [9, 10, 11].

We must notice that also other authors [19, 21] have pointed out that $\tau_{0\eta}$ is rather proportional to $\sqrt{I}$.

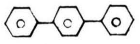
Comparison with Experiments and Discussion

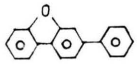
For comparison of our approach with experimental data we have chosen four similar prolate fluorescent molecules: p-terphenyl and three molecules of oxido-substituted p-oligophenylens, which were experimentally investigated by Kawski et al. [9, 10] at 296.5 K in diferent solvents with different viscosities η. From these data the values A and I were etimated by means of (3) and (3a), and the effective volumes V were obtained from the high viscosity slope of Perrin's dependence of r^{-1} on η^{-1}. The values of I obtained in this way are of the order of 10^{-40} kg · m^2 [9, 10], whereas those calculated from its geometrical structure are in the order of 10^{-43} kg · m^2 (cf. Table 1).

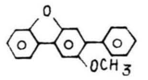
Table 1

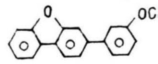
Quantities	□	×	+	△
$\langle\tau_F\rangle$ [ns]	1.11	1.31	1.38	1.30
$10^{44}\, I^{calc}_{x,y,z}$	0.438	0.523	1.041	0.731
[kg · m^2]	5.247	5.117	5.208	6.920
	5.685	5.639	6.249	7.650
τ_0 [ps]	2.32	2.32	2.44	2.70
$\tau_{0\eta}$[ps]	9 ± 3	9 ± 2	4 ± 7	4 ± 1
$10^{44} \cdot I$[kg · m^2]	91 ± 66	89 ± 51	15 ± 60	21 ± 14
$10^{30} \cdot V$[m^3]	165 ± 12	148 ± 9	211 ± 32	231 ± 5

Meaning of the symbols:

△  p-terphenyl

×  2,2′-epoxyterphenyl

+  5′-methoxy-2,2′-epoxyterphenyl

△  3″-methoxy-2,2′-epoxyterphenyl

Viscosity η [cP] of the solvents [9, 10]:

n-hexane	benzene	cyclohexane	dioxane
0.32	0.66	1.01	1.45

Parameters used: $r(0) = 0.4$ and $p = 22 \pm 7.9$.

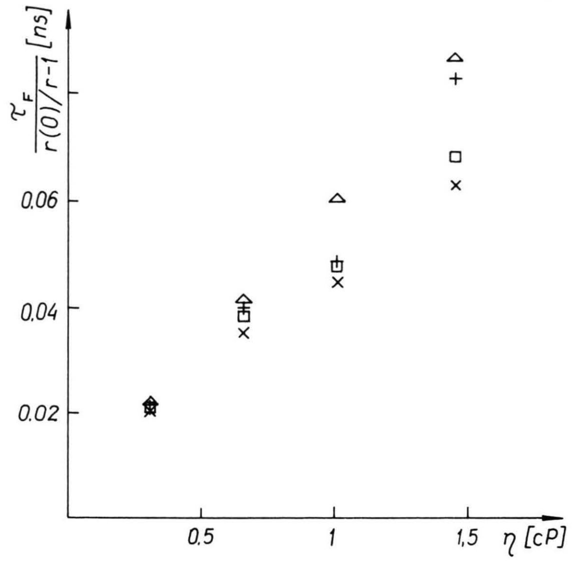


Fig. 3. $\tau_F/[r(0)/r-1]$ vs. η plot according to (12) for a low-viscosity region. Marks: experimental points taken from [9, 10].

Moreover, we must notice that the experimental data [9, 10] which we have used are not fully adequate for precise comparison. When a probe molecule is relocated from one solvent to another, its interaction with the solvent changes in a non-linear manner and so does its effective volume [23, 6]. This effect takes place also in this case.

If both conditions $\tau_F \gg \tau_0$ and low η are fulfilled, then (10) can be reduced to the form

$$\frac{\tau_F}{r(0)/r-1} = \tau_{0\eta} + \frac{V\eta}{kT}. \qquad (12)$$

This is the case for prolate molecules of oxido-substituted p-oligophenylenes in non-polar solvents.

Our results, calculated from (12) with experimental data [9, 10] are listed in Table I.

It can be seen that the calculated components I_z are almost comparable with I obtained from experiment, whereas the values of I obtained from (3) and (3a) are three orders of magnitude greater.

The effective volumes estimated from the low-viscosity region possess by about 20% lower values than those obtained from the high-viscosity region [9–11]. Such an effect was first found in light scattering experiments [23, 6] in which, however, the volumes measured were not greater than the geometrical ones. In non-polar solvents both experiments, the light scattering and the fluorescence, are in good accordance.

The results given above suggest that a single exponential memory function $K(t)$ is not adequate for the description of molecular dynamics in a liquid.

Acknowledgement

This work is supported within Research Project CPBP 01.06–2.02.

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