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POLARIZED FLUORESCENCE IN AN ELECTRIC FIELD: STEADY STATE AND TRANSIENT VALUES FOR THE FOURTH MOMENT OF THE ORIENTATION FUNCTION AT ARBITRARY FIELDS

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Steady state and time dependent expressions for the field dependence of the fourth moment of the orientation function at arbitrary fields, which are requested for the interpretation of polarisation of fluorescence in an electric field, have been obtained for permanent and induced dipole orientation. Some general features of the results and some problems connected with their application are pointed out.

1. Introduction

Changes in intensity of the polarized components of fluorescence resulting from the molecular orientation in an electrical field have been shown to be an interesting new electrooptical effect [1,2]. The main advantages compared to birefringence and dichroism [3] result from the specificity of fluorescence, from the simultaneous study of the changes in the four polarized components (V_V, H_B, V_H, H_H) and from their dependence upon not only the second but also the fourth moment of the orientation function. It is worth noting that exactly the same advantages would be associated with the observation of the change in the polarized components of Raman scattering upon orientation. Achievement of a satisfactory signal to noise ratio [4] generally requires the application of large electric field pulses. The measurements are therefore often performed outside of the region were the effects are proportional to the square of the applied field (the "Kerr" region). The field dependence of the effect can then give information on the mechanism of orientation, due either to a permanent dipole moment, to an anisotropy in electrical polarisability or to a combination of both. The expressions for the polarized components of fluorescence have been given [1,2] as a function of the two average values $\langle \sin^2\theta \rangle$ and $\langle \sin^4\theta \rangle$. The first one is directly related to the orientation factor in birefringence and dichroism $\phi = (3\langle \cos^2\theta \rangle - 1)/2$ which has already been calculated by O'Konski and al [5]. We perform here the calculation of the second one. Not only its steady state value but also its rise and decay at low and high fields have been calculated. This is for example needed to evaluate at which conditions the field free decay at higher fields can be used for polydispersity analysis [6].

2. Theory

Because of the cylindrical symmetry, the molecular orientation is fully described by the distribution $f(\theta)$ where θ is the angle between the rod axis and the direction of the applied electric field E. For long enough rod like particles, the rotational diffusion constant around a transverse axis is negligible at the time scale of the fluorescence life time τ. The rotational diffusion around the rod axis is unchanged by orientation. Under these assumptions the magnitudes of the four polarized components of fluorescence can be expressed as a function of the two averages $\langle \sin^2\theta \rangle$ and $\langle \sin^4\theta \rangle$. Their coefficients are function of the three angles χ, χ' and ψ which define the position of the absorption and emission transition moments in the

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molecular frame of reference [2]. The steady state and transient values of $\langle \sin^2\theta \rangle$ can be deduced from that of $\phi = (3\cos^2\theta - 1)/2$ the orientation factor calculated in the case of electric birefringence or dichroism. We calculate here the corresponding values of $\langle \sin^4\theta \rangle$, for the same mechanisms of orientation corresponding to the existence of:

a) a permanent dipole moment μ along the rod axis

b) an anisotropic electrical polarisability of the particle with two principal values α_1 and α_2 along and perpendicular to the rod axis. This latter situation corresponds in particular to the case of rigid polyelectrolytes. The polarisability originates then in the deformability of the counter-ion atmosphere.

2.1. Steady state orientation

The nth power average of $\sin\theta$ is defined by:

$$\langle \sin^n\theta \rangle = \frac{\int \sin^{n+1}\theta f(\theta) \mathrm{d}\theta}{\int f(\theta) \sin\theta \, \mathrm{d}\theta}, \tag{1}$$

where $f(\theta)$, the unnormalized orientation function can be simply replaced by the Boltzman factor

$$\exp\{-U(\theta)/kT\}$$

where $U(\theta)$, corresponding to the energy of the molecule in the electric field E, is given by:

$$U(\theta) = -\mu E \cos\theta - \tfrac{1}{2}(\alpha_1 - \alpha_2)E^2 \cos^2\theta. \tag{2}$$

We define as usual

$$\beta = \mu E/kT, \qquad 2\gamma = (\alpha_1 - \alpha_2)E^2/kT,$$

and perform the calculations of $\sin^4\theta$ as a function of β and γ. In a few cases we shall quote, for the easiness of comparison, the already known results for $\langle \sin^2\theta \rangle$.

2.1.1. The case of purely permanent dipole moment orientation

In the absence of polarisability anisotropy ($\gamma = 0$), the integration of (1) can be performed analytically. One finds:

$$\langle \sin^4\theta \rangle_\beta = \frac{8}{\beta^2}\left[1 - \frac{3}{\beta}\left(\coth\beta - \frac{1}{\beta}\right)\right] = \frac{8}{\beta^2}\phi_\beta, \tag{3}$$

where the index β states that the mechanism of orientation is purely due to a permanent dipole moment and ϕ_β is the corresponding orientation factor calculated by O'Konski [5].

2.1.2. The case of simultaneous permanent and induced dipole moment orientation

In the case where $U(\theta)/kT$ is a function of both β and γ (i.e. both a permanent and induced moment contribute to the orientation) the integration of (1) cannot be completely performed analytically and the results are expressed in term of the tabulated Dawson integral:

$$D(x) = \mathrm{e}^{-x^2} \int_0^x \mathrm{e}^{2t^2} \mathrm{d}t \tag{4}$$

One then finds:

$$\begin{aligned}\langle \sin^4\theta \rangle = 1 + \frac{3}{2\gamma} - \frac{\beta^2}{4\gamma^2} \\ \times \left\{1 - \frac{1}{2\gamma}[2\gamma(\mathrm{e}^{\beta} + \mathrm{e}^{-\beta}) - (\mathrm{e}^{\beta} - \mathrm{e}^{-\beta})]\right. \\ \times \left(2\sqrt{\gamma}\left[\mathrm{e}^{\beta} D\left(\frac{\beta + 2\gamma}{2\sqrt{\gamma}}\right) - \mathrm{e}^{-\beta} D\left(\frac{\beta - 2\gamma}{2\sqrt{\gamma}}\right)\right]\right)^{-1} \\ \left. + \frac{\beta^2}{2\gamma} - 1\right\} - \frac{1}{\gamma}\left\{1 + \frac{\beta^2}{4\gamma^2} - \frac{\beta}{\gamma}(\mathrm{e}^{\beta} - \mathrm{e}^{-\beta})\right. \\ \left. \times \left(4\sqrt{\gamma}\left[\mathrm{e}^{\beta} D\left(\frac{\beta + 2\gamma}{2\sqrt{\gamma}}\right) - \mathrm{e}^{-\beta} D\left(\frac{\beta - 2\gamma}{2\sqrt{\gamma}}\right)\right]\right)^{-1}\right\}.\end{aligned} \tag{5}$$

Low fields (LF) and high field (HF) expansions can be calculated and are given together with the corresponding expansions for $\langle \sin^2\theta \rangle$.

$$\begin{aligned}\text{LF} \quad \langle \sin^2\theta \rangle_{\beta,\gamma\to 0} &= \tfrac{2}{3}[1 - \tfrac{1}{15}(\beta^2 + 2\gamma) \\ &\quad - \tfrac{1}{315}(4\gamma^2 + 4\beta^2\gamma - 2\beta^4) + \ldots], \\ \langle \sin^4\theta \rangle_{\beta,\gamma\to 0} &= \tfrac{8}{15}[1 - \tfrac{2}{21}(\beta^2 + 2\gamma) \\ &\quad - \tfrac{1}{315}(4\gamma^2 + 4\beta^2\gamma - 3\beta^4) + \ldots].\end{aligned} \tag{6}$$

$$\text{HF} \quad \langle \sin^2\theta \rangle_{\beta,\gamma\to\infty} = 2/(\beta + 2\gamma),$$

$$\langle \sin^4\theta \rangle_{\beta,\gamma\to\infty} = 8/(\beta + 2\gamma)^2 = 2\langle \sin^2\theta \rangle^2. \tag{7}$$

In the case where the orientation is due only to an

Table 1
Values of the orientational averages for permanent (β) and induced (γ) dipole moment orientation.

β	$\langle\sin^2\theta\rangle$	$\langle\sin^4\theta\rangle$	$\sqrt{\gamma}$	$\langle\sin^2\theta\rangle$	$\langle\sin^4\theta\rangle$
0	0.666666	0.533333	0	0.666666	0.533333
0.1	0.666223	0.532826	0.1	0.665777	0.532317
0.2	0.664896	0.531310	0.22	0.662200	0.528237
0.3	0.662701	0.528803	0.30	0.658599	0.524136
0.4	0.659562	0.525334	0.40	0.652223	0.516913
0.6	0.651196	0.515683	0.50	0.643934	0.507540
0.8	0.639852	0.502780	0.60	0.633628	0.495966
1.00	0.626071	0.487153	0.70	0.621231	0.482141
1.20	0.610340	0.469386	0.80	0.606663	0.466028
1.40	0.593156	0.450067	0.90	0.589855	0.447613
1.60	0.574986	0.429754	1.00	0.570769	0.426923
1.80	0.556252	0.408942	1.20	0.525838	0.379141
2.00	0.537315	0.388056	1.40	0.472764	0.324370
2.50	0.490857	0.337564	1.60	0.413945	0.265866
3.00	0.447758	0.291879	1.80	0.353284	0.208200
3.50	0.409210	0.252211	2.0	0.295373	0.156138
4.00	0.375336	0.218498	2.23	0.235734	0.106454
4.50	0.345789	0.190150	2.83	0.137931	0.038793
5.00	0.320036	0.166383	3.16	0.107272	0.023263
5.50	0.297533	0.146433	4.47	0.051445	0.005304
6.00	0.277782	0.129268	5	0.040895	0.003349
7.00	0.244898	0.103290	6.32	0.025334	0.001284
8.00	0.218750	0.083984	7.07	0.020211	0.000817
9.00	0.197531	0.069502	10	0.010051	0.000202
10.00	0.180000	0.058400	14.14	0.005013	0.000050
15.00	0.124444	0.028919	∞	0	0
20.00	0.095000	0.017150			
∞	0	0			

induced dipole moment, the average (which will then be designated by an index γ) can be calculated making $\beta = 0$ in relation (5).

Numerical calculations in the case $\langle\sin^4\theta\rangle_\beta$ and $\langle\sin^4\theta\rangle_\gamma$ have been performed. They are reported in table 1 together with the corresponding values of $\langle\sin^2\theta\rangle$ for convenience for further numerical applications. Since the quantities of interest in the interpretation of electrooptic effects are often only the relative changes:

$$(\langle\sin^2\theta\rangle_{E=0} - \langle\sin^2\theta\rangle)/\langle\sin^2\theta\rangle_{E=0} = 1 - \tfrac{3}{2}\langle\sin^2\theta\rangle = \phi,$$

$$(\langle\sin^4\theta\rangle_{E=0} - \langle\sin^4\theta\rangle)/\langle\sin^4\theta\rangle_{E=0} = 1 - \tfrac{15}{8}\langle\sin^4\theta\rangle = \Delta, \quad (8)$$

it is their values, which vary from 0 to 1 which have been reported in figs. 1 and 2. It is interesting to see to what extent these relative changes can be represented by a simple E^2 dependence at low field and by their asymptotic expansion at high fields. For that purpose dotted lines corresponding in fig. 1 to the HF expansion and in fig. 2 to the LF expansion have been drawn for comparison with the exact result. As already observed by O'Konski for ϕ_γ, Δ_γ increases more rapidly than predicted by the first term in the LF expansion. From an experimental point of view however, an essentially E^2 dependence is expected up to 50% of the electrooptical effect at saturation for induced moment orientation, while a pronounced curvature should already be present at 15% of the effect at saturation in the case of permanent moment orientation.

2.2. Transient effect – Rise

A general formulation of the time dependent orientation function $f(\theta, t)$ following the sudden application

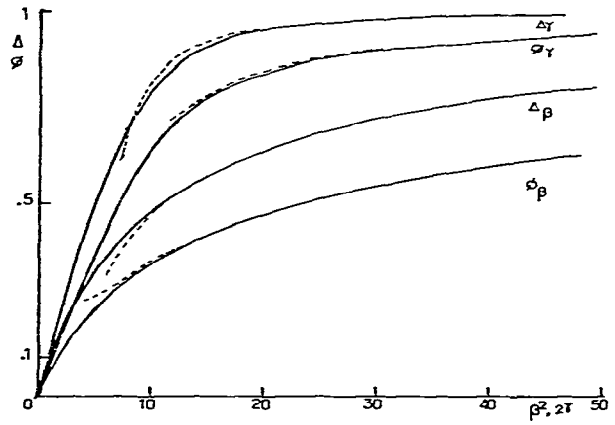

Fig. 1. The "degrees of orientation" ϕ and Δ as a function of the square of the electric field for induced ($2\gamma = (\alpha_1 - \alpha_2)E^2/kT$) and permanent ($\beta = \mu E/kT$) moment orientation. Dotted lines correspond to the asymptotic expansions at high fields (relation 7).

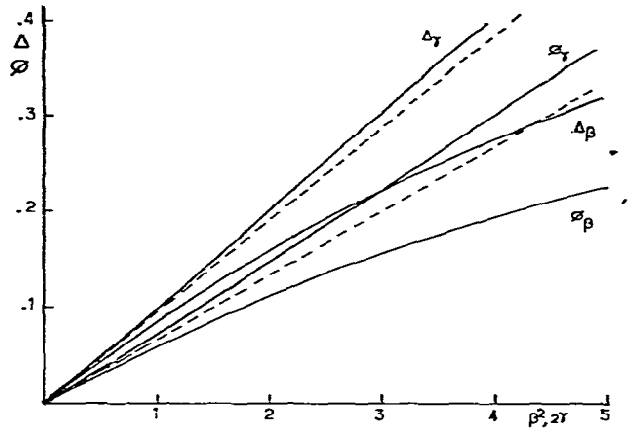

Fig. 2. Same as fig. 1. Detail of the low field behaviour. Dotted lines correspond to the first term in the low field expansions (relation 6).

of an electric field has been given for a rod-like particle by Nishinari and Yoshioka [7]. Using their formulation in term of the operator $\hat{F}$

$$f(\theta,t) = \exp(\hat{F}Dt)f(\theta,0) = \frac{1}{4\pi}\sum_{n=0}^{\infty}\frac{D^n t^n}{n!}\hat{F}^n,$$

$$\hat{F} = (1-u^2)\frac{\partial^2}{\partial u^2} - 2u\frac{\partial}{\partial u} - (1-u^2)(\beta+\gamma u)\frac{\partial}{\partial u} + 2\beta u + \gamma(3u^2-1)/2, \qquad (9)$$

where $u = \cos\theta$ and D is the rotational diffusion constant around the transverse axis of the particle, one calculates the time dependence of ϕ and Δ in terms of a serie expansion in powers of Dt (the superscript tr stands here for "transient-rise")

$$\phi^{tr} = \tfrac{2}{5}Dt + (\beta^2 - 6\gamma + \tfrac{4}{7}\gamma^2)D^2t^2 - (\tfrac{8}{3}\beta^2 - 12\gamma + \tfrac{20}{21}\beta^2\gamma + \tfrac{16}{7}\gamma^2 + \tfrac{16}{21}\gamma^3)D^3t^3 + \dots,$$

$$\Delta^{tr} = \tfrac{8}{7}\gamma Dt + (\beta^2 - 6\gamma)D^2t^2 - (\tfrac{8}{7}\beta^2 - 12\gamma + \tfrac{16}{9}\beta^2\gamma - \tfrac{8}{3}\gamma^2 + \tfrac{32}{33}\gamma^3)D^3t^3 + \dots. \qquad (10)$$

More exact expressions can be calculated from the analytical expressions of the time dependent orientation function $f(\theta, t)$ given by several authors in special cases.

2.2.1. Small orientation at low field

Using the expression of $f(\theta, t)$ given by Benoit [8]. one gets:

$$\Delta^{tr}_{\beta,\gamma} = \tfrac{2}{21}[\beta^2 + 2\gamma - \tfrac{3}{2}\beta^2 e^{-2Dt} + (\beta^2/2 - 2\gamma)e^{-6Dt}] \qquad (11)$$

2.2.2. Pure induced dipole moment orientation at high fields

From the expression of $f(\theta, t)$ given by Schwarz [9] one calculates:

$$\langle\sin^4\theta\rangle^{tr}_{\gamma} = \frac{e^{4\gamma Dt} - 4}{2(e^{4\gamma Dt} - 1)^2} \times \left[e^{4\gamma Dt}\frac{\operatorname{arctg}(e^{4\gamma Dt} - 1)^{1/2}}{(e^{4\gamma Dt} - 1)^{1/2}} + \frac{e^{4\gamma Dt} + 2}{e^{4\gamma Dt} - 4}\right]. \qquad (12)$$

One should remark that the short time expansion

$$\Delta^{tr}_{\gamma} = \tfrac{8}{7}\gamma Dt - \tfrac{128}{231}\gamma^3 D^3 t^3 + \dots \qquad (13)$$

contain only, by contrast with (10), terms of the form $\gamma^n D^n t^n$.

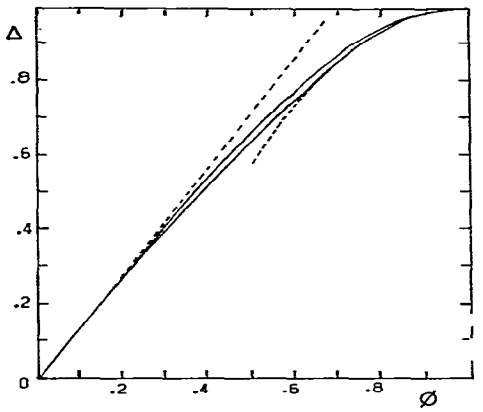

Fig. 3. Δ as a function of ϕ for β and γ orientation. The dotted lines correspond to the first term in respectively the low field (6) and high field (7) expansions.

2.2.3. Pure permanent dipole orientation at high fields

$f(\theta, t)$ has been given by O'Konski [5]. It leads to:

$$\Delta_{\beta}^{tr} = \frac{16e^{2\beta Dt}}{3(e^{2\beta Dt}-1)^2} \times \left[1 + \frac{12e^{2\beta Dt}}{(e^{2\beta Dt}-1)^2} - \frac{12\beta Dt(e^{4\beta Dt}+e^{2\beta Dt})}{(e^{2\beta Dt}-1)^3}\right] \quad (14)$$

The short time expansion gives:

$$\Delta_{\beta}^{tr} = \tfrac{4}{7}\beta^2 D^2 t^2 - \tfrac{4}{21}\beta^4 D^4 t^4 + \tfrac{163}{2310}\beta^6 D^6 t^6 + \ldots . \quad (15)$$

where the same observation as in sect. 2.2.2. applies.

2.3. Transient effect – Free decay

Expressions of the time dependent function $f(\theta, t)$ following the sudden switch off of the electric field have only been given in the two limiting cases of small and complete initial orientation. They appear as series in Legendre polynomials with terms proportional to $P_n(\cos\theta)\exp\{-n(n+1)Dt\}$ [8]. Since $\sin^4\theta$ can be expressed as a combination of P_2 and P_4:

$$\sin^4\theta = \tfrac{56}{105} - \tfrac{80}{105}P_2(\cos\theta) + \tfrac{8}{35}P_4(\cos\theta),$$

it is a simple matter, using the orthogonality of the Legendre polynomials to obtain:

$$\Delta^{td}_{\beta,\gamma\to 0} = \tfrac{2}{21}(\beta^2+\gamma)e^{-6Dt}, \quad (16)$$

$$\Delta^{td}_{\beta,\gamma\to\infty} = \tfrac{10}{7}e^{-6Dt} - \tfrac{3}{7}e^{-20Dt}, \quad (17)$$

where the superscript td stands here for "transient-decay".

3. Discussion

Several remarks can be made on the practical use of the results in the interpretation of the changes in the intensity of polarized components of fluorescence in an electric field.

3.1. Steady state orientation

It is often difficult, from an experimental point of view to reach complete saturation of the electro-optical effect, and there is a large difference in the approach of saturation for induced and dipole moment orientation. Fig. 1 shows that this difference is found for Δ as well as for ϕ, but that Δ increases more rapidly than ϕ and reaches values close to 1 at lower fields. This should make the field dependence of the steady state changes in polarized fluorescence an interesting mean to differentiate between the two orientation mechanisms.

A particular advantage of polarized fluorescence is the observation of the four polarized components of fluorescence. There exists in the Kerr region, a relation between their changes which is related to the proportionality between ϕ and Δ [2]. This relation has been found experimentally to hold at higher fields [2,4]. This can be understood considering fig. 3 where it is shown that the low field proportionality remains approximately verified up to $\Delta \sim 0.5$, whatever the mechanisms of orientation.

Since it has been found that in the high field approximation, whatever the mechanism of orientation $\langle\sin^4\theta\rangle = 3\langle\sin^2\theta\rangle^2$, it is not very surprosing that the relation between ϕ and Δ is not very sensitive to the mechanism of orientation. This might however be useful to obtain their absolute values when the magnitude of the effect at saturation of the orientation is not experimentally or theoretically accessible.

3.2. Transient effects

The time dependence of Δ following the sudden application of an electric field shows the same difference between permanent and induced dipole moment orientation as that of ϕ. Relation (10) shows that for permanent dipole moment orientation the initial slope is zero while it is proportional to γD for induced dipole moment orientation. The transient changes in the polarized components of fluorescence can therefore help to characterize the type of orientation mechanism.

At low orientations, the field free decay following the switch off of the field is exponential with the same relaxation time $(6D)^{-1}$ for both ϕ and Δ. The initial slope of the decay can therefore be directly used to obtain a value of D. But one must be very cautious when working at higher fields (a normal trend to increase the signal to noise ratio). Indeed relation (17) shows that, at full orientation, the decay of Δ is highly non exponential with no linear term in t in the short time expansion. This makes the experimental determination of the "initial slope" for the measurement of D very questionable at higher fields.

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