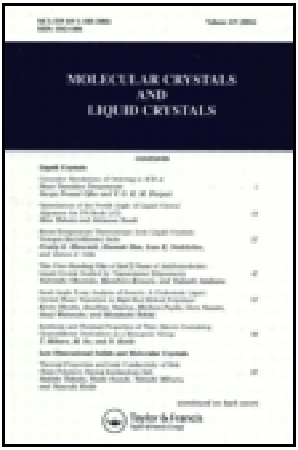

Molecular Crystals and Liquid Crystals

Director Reorientation Due to Dye Photoabsorption

Matteo Stocchero [a] & Giorgio J. Moro [a]

[a] Dipartimento di Chimica Fisica, Università di Padova, Via Loredan 2, Padova, 35131, Italy

Version of record first published: 18 Oct 2010

To cite this article: Matteo Stocchero & Giorgio J. Moro (2003): Director Reorientation Due to Dye Photoabsorption, Molecular Crystals and Liquid Crystals, 395:1, 269-281

To link to this article: http://dx.doi.org/10.1080/15421400390193800

Mol. Cryst. Liq. Cryst., Vol. 395, pp. [269]/99–[281]/111, 2003
Copyright © Taylor & Francis Inc.
ISSN 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400390193800

DIRECTOR REORIENTATION DUE TO DYE PHOTOABSORPTION

Matteo Stocchero and Giorgio J. Moro
Dipartimento di Chimica Fisica, Università di Padova
Via Loredan 2, 35131 Padova, Italy

The addition of small quantities of an absorbing dye can modify the optical properties of liquid crystals, in particular by producing a photo-induced torque reorienting the director. Such an effect is modelled by including in the free energy the contribution of dye-solvent electrostatic interactions between the molecular charges and the solvent polarisation. The system evolution is described through the torque acting on the director and the diffusion equations for the orientational distributions of the dye in the ground and the excited states. In the presence of a time scale separation between molecular variables (orientation) and collective properties (director), an explicit relation is derived for the dye photo-induced torque, which appears to be compatible with the experimental findings.

Keywords: rotational diffusion; nematic director dynamics; optical properties of liquid crystals; dye-induced torque

INTRODUCTION

It is well known that the interaction of the electric field **E** of polarised light with a birefringent transparent medium produces an optical torque which, in the case of a nematic liquid crystal, can be detected through the reorientation of the director like in the Freedericksz transitions. Its description taking into account the permittivity anisotropy $\Delta\varepsilon^{opt} = \varepsilon_{\parallel}^{opt} - \varepsilon_{\perp}^{opt}$ at the frequency of the transmitting light, leads to the following relation for the optical torque [1,2]

$$\boldsymbol{\tau}_{opt} = \Delta\varepsilon^{opt}\overline{E^2}(\mathbf{n}\cdot\mathbf{e})\mathbf{n}\times\mathbf{e} \tag{1}$$

where **n** and **e** denote the unit vectors along the nematic director and

---

This work has been supported by the EU Commission through the TMR Contract FMRX CT 97 0121, and by the Italian MIUR through PRIN ex 40%. We acknowledge also the stimulating discussions with A. Ferrarini and the help of A. di Matteo for the ZINDO/S calculations.

electric field of the light, respectively, while $\overline{E^2}$ is the time average of the squared electric field.

Some years ago Janossy and coworkers found that the director photoalignment was strongly affected by the addition of a dye absorbing at the wavelength of the probing light [3,4]. In particular small concentrations of dyes of anthraquinone type were sufficient to reduce the optical Freedericksz threshold by one or two orders of magnitude. These investigations pointed out that this effect requires an explanation completely different from that of the optical torque Eq. (1). Theoretical descriptions of the dye-induced torque have been proposed by analysing the rotational diffusion of the dye under the hypothesis that the interactions with the nematic solvent change drastically during the excitation [5,6]. Still a satisfactory explanation is not available for the origin of such a change of interactions with the solvent. For instance the formation of strong hydrogen bonds has been invoked for antraquinone dyes in the excited state [7]. On the other hand the experimental data reported by Marrucci et al. [8] show that the effects of dye absorption are strongly dependent on the dielectric properties of the nematic solvent. It should be also evident that the lack of a clear identification of the mechanisms driving the director reorientation hampers the developments on the investigations and the applications of this process, as long as the relation between the structure and the properties of the dye on the one hand, and photo-induced effects on the other hand, remains uncertain.

In the effort of clarifying the physical origin of this process, we have developed a stochastic model for the dynamical coupling of dye and director reorientation due to electrostatic interactions. The basic idea is that the transition to the excited state produces a significant reorganisation of the charge density of the dye, and this modifies the electrostatic interactions with the nematic solvent represented as a dielectric continuum [9,10]. It will be shown that in suitable conditions this produces a torque acting on the director. In order to clearly present the physical interpretation of the problem with the minimal formal treatment, we shall consider a simplified situation for a nematic solvent without anisotropy of the static permittivity, $\varepsilon^s_{||} = \varepsilon^s_{\perp}$. Such a condition can be experimentally met by using a suitable mixture of nematics with opposite permittivity anisotropies. In this case the relation between the absorption-induced torque and dye properties becomes particularly simple so providing a direct insight on the molecular mechanisms controlling the process. On the other hand the methodology here presented can be generalised to solvents with dielectric anisotropy, as it will be shown in a future work [11].

The paper is organised as follows. In the next section the model is specified according to the time evolution equations for the director and the dye orientational distributions. A key ingredient is the free energy density which should include the contribution of dye-solvent interactions. In the following section a coarse grained solution is derived in the presence of a time scale separation between director dynamics and molecular orientational relaxation. This leads to an analytical relation for the torque due to the dye photoabsorption. This results, together a theoretical estimate of the effects for a specific anthraquinone dye, is discussed in the conclusion section.

THE MODEL

Before to examine the effects of dye absorption, we have to describe the dynamics of the director. In a typical experiment for the measurement of the Fredericksz threshold, the flow of nematic material is negligible. Therefore, the Ericksen-Leslie equations [12] can be reduced to the time evolution of the director field $\mathbf{n}(\mathbf{r}, t)$ only

$$\frac{\partial \mathbf{n}}{\partial t} = -\frac{1}{\gamma}\mathbf{n} \times \boldsymbol{\tau} \tag{2}$$

where γ is the rotational viscosity coefficient. In principle the torque $\boldsymbol{\tau}$ should include both the elastic contribution and the effects of the solvent interactions with the dye and with the electric field of the propagating light. In order to concentrate our analysis on the dye photoabsorption effects, we neglect the purely elastic contribution by considering an homogeneous sample with the director $\mathbf{n}(t)$ independent of the position in correspondence of a nematic cell of infinite thickness. Then, in the absence of director gradients, the torque can be specified according to the director derivative of the free energy density f of the nematic phase [13]

$$\boldsymbol{\tau} = -\mathbf{n} \times \frac{\partial f}{\partial \mathbf{n}} \tag{3}$$

The electric field $\mathbf{E} = E\mathbf{e}$ of the light polarised along the direction $\mathbf{e}$ has a twofold effect: it produces a polarisation of the sample and it induces transitions to the excited state on the dye molecules doping the nematic host. The latter process modulates the solvent-dye interactions in general dependent on the electronic state (either ground or first excited state) occupied by the dye. Correspondingly we separate in the free energy density the two effects

$$f = f_{opt} + f_{dye} \tag{4}$$

with f_{dye} and f_{opt} denoting the dye-solvent contribution and the polarisation contribution of optical origin, respectively. The latter can be specified according to the optical permittivity [14]

$$f_{opt} = -\frac{1}{2}\overline{E^2}[\varepsilon_{\perp}^{opt} + \Delta\varepsilon^{opt}(\mathbf{n}\cdot\mathbf{e})^2] \tag{5}$$

so recovering from Eq. (3) the optical torque Eq. (1) which would be acting in the absence of dye effects.

In order to evaluate f_{dye}, let us first examine the interaction potential $V_i(\boldsymbol{\Omega})$ between a dye molecule and its surrounding. Because of the anisotropic character of the solvent, it depends on the molecular orientation with respect to the director. In the following the dye orientation will be specified according to the Euler angles $\boldsymbol{\Omega} = (\alpha, \beta, \gamma)$ for the rotation from the Director Frame (DF) having the z axis along $\mathbf{n}$, to the Molecular Frame (MF). The interaction potential $V_i(\boldsymbol{\Omega})$ depends also on the electronic state of the dye, either ground state, $i = 0$, or excited state $i = 1$. As done in the analysis of the orientational order of solutes in nematics [9,10], one can separate in the potential a short range part $V^{sr}(\boldsymbol{\Omega})$ due to dispersion and excluded volume interactions controlled by the molecular shape, from the electrostatic part V_i^{el} due to the solvent polarisation induced by the molecular charges

$$V_i(\boldsymbol{\Omega}) = V^{sr}(\boldsymbol{\Omega}) + V_i^{el} \tag{6}$$

We assume that the molecular shape does not change because of the transition, so that short range potential can be considered independent of the electronic state. Of course this model cannot be applied to azobenzene dyes for which conformational transitions driven by the excitation of the electronic state have an important role [15]. We shall confine our analysis to rigid dyes whose structure is nearly independent of the electronic state, like some of the anthraquinone dyes. On the contrary a strong dependence on the electronic state is expected for the electrostatic contributions, since the transition to the excited state can modify to a large extent the molecular charge distribution and correspondingly the induced polarisation of the solvent. In ref. [9,10] it is shown how to calculate these electrostatic energies in the framework of the continuum representation of the solvent by solving the Laplace-Poisson equation for a given set of molecular cavity, charge distribution and static permittivity tensor $\boldsymbol{\varepsilon}^s$. The resulting electrostatic energy has in general an explicit orientational dependence controlled by the static permittivity anisotropy $\Delta\varepsilon^s = \varepsilon_{||}^s - \varepsilon_{\perp}^s$. In order to simplify the analysis of the dynamical problem, in the following we shall consider the simpler situation of electrostatic energies V_i^{el} independent of dye orientation, in correspondence of solvents with isotropic dielectric properties: $\varepsilon_{||}^s - \varepsilon_{\perp}^s$. Experimentally this can be realised by employing a suitable mixture of nematogens with opposite permittivity anisotropies, like for the "magic mixtures" used for excluding solvent polarisation contributions in the measurement of orientational order parameters [16].

By considering the solvent as a continuum surrounding the dye molecules, one can evaluate the dye contribution f_{dye} to the free energy density simply by adding the interaction potential $V_i(\boldsymbol{\Omega})$ for each solute. By introducing the molar density of the i-th state $c_i(\boldsymbol{\Omega}, t)d\boldsymbol{\Omega}$ (moles for unit volume) having an orientation within $\boldsymbol{\Omega}$ and $\boldsymbol{\Omega} + d\boldsymbol{\Omega}$ at a given time t, such a free energy is given as

$$f_{dye} = N_{\mathrm{Avog}} \sum_{i=0,1} \int d\boldsymbol{\Omega}\ c_i(\boldsymbol{\Omega}, t) V_i(\boldsymbol{\Omega}) \tag{7}$$

where the Avogadro number N_{Avog} has been introduced for converting a molar density to a number of molecules for unit volume. This relation has a prominent role in our model since it connects molecular distributions, i.e. the orientational densities $c_i(\boldsymbol{\Omega}, t)$, with the evolution of a collective property like the director through the torque to be evaluated according to Eq. (3).

Different processes have to be considered in order to describe the time evolution of the orientational densities $c_i(\boldsymbol{\Omega}, t)$: i) the molecular rotational diffusion, ii) the excitation due to the polarized light and iii) the spontaneous decay from the excited state. Let us analyse separately each process. The simplest description of the rotational diffusion is provided by the Smoluchowski-Fokker-Planck equation for anisotropic media [17,18] by using the following time evolution operator

$$\boldsymbol{\Gamma} = -\mathbf{M}^{tr} \cdot \mathbf{D} P_{eq}(\boldsymbol{\Omega}) \mathbf{M} P_{eq}(\boldsymbol{\Omega})^{-1} \tag{8}$$

where $\mathbf{M}$ is the infinitesimal rotation operator and $\mathbf{D}$ is the diffusion tensor. $P_{eq}(\boldsymbol{\Omega})$ denotes the equilibrium orientational distribution as derived from the interaction potential Eq. (6) interpreted as a mean field potential for the dye molecule

$$P_{eq}(\Omega) \propto \exp\{-V_i(\Omega)/k_B T\} \propto \exp\{-V^{sr}(\Omega)/k_B T\} \tag{9}$$

and with normalisation

$$\int d\Omega\, P_{eq}(\Omega) = 1 \tag{10}$$

Notice that ground and excited states are characterised by the same equilibrium distribution as long as the electrostatic contribution V_i^{el} is independent of the orientation. Of course, this condition is not satisfied in the presence of an anisotropic permittivity, $\Delta\varepsilon^s \neq 0$, in which case different evolution operators have to be introduced for the ground state and the excited state [11].

The excitation rate of dye molecules depends on the projection of the electrical field along the direction $\mathbf{u} = \boldsymbol{\mu}_{ge}/|\boldsymbol{\mu}_{ge}|$ of the transition dipole moment $\boldsymbol{\mu}_{ge}$ according to the relation

$$a(\Omega) = \frac{\Lambda \overline{E^2}}{N_{Avog.}} (\mathbf{u} \cdot \mathbf{e})^2 \tag{11}$$

where Λ is the absorption cross section [5]. Finally the transition from the excited state is described according to the decay rate k_e. By including all these processes, the equations for the time evolution of the two orientational densities become

$$\frac{\partial}{\partial t} c_0(\Omega, t) = -[\Gamma + a(\Omega)] c_0(\Omega, t) + k_e c_1(\Omega, t) \tag{12a}$$

$$\frac{\partial}{\partial t} c_1(\Omega, t) = -[\Gamma + k_e] c_1(\Omega, t) + a(\Omega) c_0(\Omega, t) \tag{12b}$$

In conclusion the rotational dynamics of the director due to dye photoabsorption can be analysed by solving the time evolution equations (2) for the director and (12) for the dye orientational densities, which are coupled through the torque $\boldsymbol{\tau}$ Eq. (3) with the free energy density given by Eq. (7).

THE COARSE GRAINED SOLUTION

Because of the collective nature of the director $\mathbf{n}$, its evolution is characterised by a time scale τ_n much longer than the typical relaxation time τ_Ω for orientational diffusion of the dye (say milliseconds versus one hundred picoseconds). This allows one to introduce a coarse grained representation of the system dynamics by considering its time evolution for times t much longer than the molecular relaxation time, but still shorter than those required to modify significantly the director orientation

$$\tau_n \gg t \gg \tau_\Omega \tag{13}$$

In these conditions, the excited state and the ground state should attain a stationary orientational densities $c_i(\Omega)$ with respect to the director. By neglecting the time derivatives, $\partial c_i/\partial t \cong 0$, and by introducing the overall $c(\Omega)$ and the difference $\Delta c(\Omega)$ orientational densities

$$c(\Omega) \equiv c_0(\Omega) + c_1(\Omega) \tag{14a}$$

$$\Delta c(\Omega) \equiv c_0(\Omega) - c_1(\Omega) \tag{14b}$$

one obtains from the two independent linear combinations of Eq. (12) the following system of equations

$$\Gamma c(\Omega) = 0 \tag{15a}$$

$$\Gamma \Delta c(\Omega) + a(\Omega)[c(\Omega) + \Delta c(\Omega)] - k_e[c(\Omega) - \Delta c(\Omega)] = 0 \tag{15b}$$

Since the stationary solution of the diffusion operator Eq. (8) is proportional to $P_{eq}(\Omega)$, one derives the following explicit solution of Eq. (15a) by taking into account that the orientational densities are expressed as number of moles for unit volume

$$c(\Omega) = C_{dye} P_{eq}(\Omega) \tag{16}$$

where C_{dye} is the dye concentration (number of moles for unit volume). Then, by substituting this result into Eq. (15b), one can find the explicit solution also for the difference in density

$$\Delta c(\Omega) = C_{dye}[\Gamma + a(\Omega) + k_e]^{-1}[k_e - a(\Omega)]P_{eq}(\Omega) \tag{17}$$

where the inverse of an operator has to be evaluated. Now the dye contribution to free energy density can be calculated from Eq. (7) so obtaining

$$\begin{aligned} f_{dye} = & \frac{C_{dye} N_{\mathrm{Avog}}}{2} \{ 2\overline{V^{sr}} + V_0^{el} + V_1^{el} \\ & - \Delta V^{el} \int d\Omega [\Gamma + a(\Omega) + k_e]^{-1} [k_e - a(\Omega)] P_{eq}(\Omega) \} \end{aligned} \tag{18}$$

where

$$\Delta V_{el} \equiv V_1^{el} - V_0^{el} \tag{19}$$

is the difference in the electrostatic energy between excited and ground state, while

$$\overline{g} \equiv \int d\Omega g(\Omega) P_{eq}(\Omega) \tag{20}$$

denotes the orientational average of a function $g(\Omega)$. Notice that the dependence on the light intensity is brought by the absorption rate $a(\Omega)$ Eq. (11).

Let us examine the dependence on the light intensity through the power series expansion on the electric field of the free energy density

$$f = f_{opt} + f_{dye} = \sum_{n=0}^{\infty} f^{(n)} \overline{E^2}^n \tag{21}$$

The zero-th order term, that is the free energy in the absence of photoexcitation, is given as

$$f^{(0)} = f_{dye}^{(0)} = C_{dye} N_{Avog.} (\overline{V_{sr}} + V_0^{el}) \tag{22}$$

In its derivation we have used the following property of differential operators like Γ:

$$\int d\Omega(\Gamma + s)^{-1} \cdots = s^{-1} \int d\Omega \cdots \tag{23}$$

for any constant s. It can verified from the series expansion of $(\Gamma + s)^{-1}$ by taking into account a constant function in the stationary solution of the adjoint operator Γ^{+}.

For the analysis of photo-induced effects, it is sufficient to truncate the series expansion Eq. (21) at the first order, so obtaining

$$f \approx f^{0)} + f_{opt} + f^{(1)}_{dye}\overline{E^2} \tag{24}$$

with

$$f^{(1)}_{dye} = \frac{C_{dye}\Lambda\Delta V^{el}}{k_e}\overline{(\mathbf{u}\cdot\mathbf{e})^2} \tag{25}$$

while the optical contribution f_{opt} Eq. (5) has an intrinsic linear dependence on $\overline{E^2}$. In deriving Eq. (25) we have employed the following relation

$$[\Gamma + a(\Omega) + k_e]^{-1} \approx [\Gamma + k_e]^{-1} - [\Gamma + k_e]^{-1}a(\Omega)[\Gamma + k_e]^{-1} \tag{26}$$

as the first order expansion with respect to $a(\Omega)$ of the operator at the l.h.s.

In order to specify the angular dependence of the free energy density, we introduce the Electric Field Frame EF having the z axis along the vector $\mathbf{e}$, with the following scheme describing the rotations with respect to the Molecular Frame MF and to the Director Frame DF

$$\begin{tikzcd} & \text{DF} \arrow[dr, "\Omega"] & \\ \text{EF} \arrow[ur, "\Xi"] \arrow[rr, "\Psi"] & & \text{MF} \end{tikzcd}$$

By choosing the z axis of the molecular frame MF along the direction $\mathbf{u}$ of the transition dipole moment, one can specify the angular dependence of $(\mathbf{u}\cdot\mathbf{e})^2$ through a Wigner function [19]

$$(\mathbf{u}\cdot\mathbf{e})^2 = \frac{1}{3} + \frac{2}{3}D^2_{0,0}(\Psi) = \frac{1}{3} + \frac{2}{3}\sum_p D^2_{0,p}(\Xi)D^2_{p,0}(\Omega) \tag{27}$$

where the last relation derives from the decomposition of Wigner functions in a sequence of two rotations [19]. In the orientational average of Eq. (27) only the $p = 0$ term survives because of the axial symmetry of the nematic phase, so obtaining the following relation for the dye contribution

$$f^{(1)}_{dye} = \frac{C_{dye}\Lambda\Delta V^{el}}{k_e}\{1/3 + [(\mathbf{e}\cdot\mathbf{n})^2 - 1/3]\overline{D^2_{0,0}(\Omega)}\} \tag{28}$$

with an explicit dependence on the angle between electric field and director.

Finally, by performing the derivative according to Eq. (3), the torque acting on the director is derived

$$\boldsymbol{\tau} = \boldsymbol{\tau}_{opt} + \boldsymbol{\tau}_{dye} \tag{29}$$

with the optical torque already specified by Eq. (1), while the dye-induced torque has the following explicit form

$$\boldsymbol{\tau}_{dye} = -2\frac{C_{dye}\Lambda\Delta V^{el}}{k_e}\overline{D^2_{0,0}(\boldsymbol{\Omega})}(\mathbf{n}\cdot\mathbf{e}) \quad \mathbf{n}\times\mathbf{e} \tag{30}$$

This is the main result of our analysis pointing out that the dye photo-induced torque has the same angular dependence of the standard optical torque Eq. (1). Of course the proportionality factor is completely different, since it depends on the dye concentration and the lifetime $1/k_e$ of its excited state, on its absorption coefficient through the parameter Λ, on the difference ΔV^{el} of dielectric polarisation energy between excited and ground states, and on the order parameter $\overline{D^2_{0,0}(\boldsymbol{\Omega})}$ along the direction $\mathbf{u}$ of the transition dipole moment. The latter parameter can be specified according to standard ordering matrix $\mathbf{S}$ as [13]

$$\overline{D^2_{0,0}(\boldsymbol{\Omega})} = \mathbf{u}\cdot\mathbf{S}\mathbf{u} \tag{31}$$

It should be stressed that no dependence on the diffusion rotational coefficient is recovered from the previous treatment. This, however, is a consequence of considering a nematic solvent with isotropic static dielectric properties. Without this assumption, electrostatic contributions $V_i^{el}(\boldsymbol{\Omega})$ with an explicit angular dependence are recovered [9,10], and this leads to a torque dependent on the diffusion coefficients [11].

CONCLUDING REMARKS

The main objective of the present communication was to demonstrate that the change of solvent polarisation due to charge redistribution in the dye molecule after the electronic transition, can represent a simple and direct explanation of the effect discovered by Janossy and co-workers [3,4]. Indeed, as shown in the previous section, this hypothesis leads to a torque acting on the director with the same angular dependence that has been found experimentally.

On the other hand, this interpretation of the photoabsorption effects can be justified also on a more qualitative ground by examining the electrostatic interactions between the dye and the nematic solvent. In order to simplify the matter, let us consider a dye with an axial elongated shape

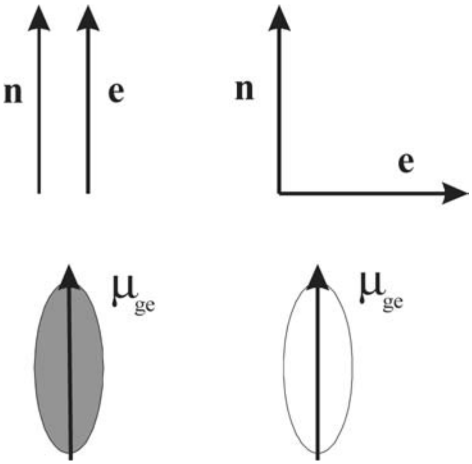

FIGURE 1 Interpretation of dye absorption-effects for the director parallel (left hand side) or perpendicular (right hand side) to the electric field.

(an ellipsoid in Fig. 1) having the transition dipole moment $\boldsymbol{\mu}_{ge}$ along the symmetry axis. Moreover we assume that the electrostatic energy V_1^{el} for the excited state is larger in magnitude than V_0^{el} for the ground state, say because of a larger dipole moment of the charge distribution in the excited state. Since both these electrostatic energies are negative (the dielectric polarisation produces a decrease of energy), the difference ΔV^{el} in electrostatic energies is negative. Then, in the limit of a dye perfectly aligned with respect to the director (as represented in Fig. 1), one can easily figure out the energetic effects of the photoabsorption.

Let us consider the case when the electric field is orthogonal to the director (right hand side of Fig. 1). As long as the electric field and the transition dipole moment are orthogonal, there are no transitions and the electrostatic interactions are taken into account by the contribution V_0^{el} of the ground state. On the contrary some dye molecule will be excited when the electric field and the director (and the transition moment as well) are parallel (left hand side of Fig. 1, with the shadowing of the dye meant to represent the light absorption). Correspondingly there will be a lowering of the electrostatic energy, and of the free energy density as well, proportional to ΔV^{el} and to the number of dye molecules in the excited state. Therefore in this case the equilibrium state of the system would be that with a complete alignment between director and electric field. If this is not the starting condition of the sample, the angular gradient of the free energy would generate a torque reorienting the director toward the equilibrium state. Such a qualitative analysis is easily extended to other simple situations, say for $\Delta V^{el} > 0$ and/or $\boldsymbol{\mu}_{ge}$ orthogonal to the long molecular axis. On the other hand, Eq. (30) supplies the interpretation of the photoinduced torque without the simplifying conditions previous invoked.

In order to demonstrate that our model is not only compatible with the experimental findings, but also provides an effective description of the process, an estimate of the dye-induced torque is necessary and we shall specifically consider the case of 1AAQ (1-amino-anthraquinone) dye dissolved in the liquid crystal E7. For a fully quantitative analysis, an accurate evaluation of the electrostatic energies V_0^{el} and V_1^{el} would be required on the basis of the molecular charge distributions in the two states. This will be done in a forthcoming contribution [11] by employing methods introduced in ref. [9,10]. Here we perform a simplified evaluation in order to show that the predicted dye-induced effect has the correct order of magnitude. In particular we estimate the electrostatic energies by using the model of dipole moments at the centre of spherical cavity of radius R [20], so that

$$\Delta V^{el} = \frac{1}{4\pi\varepsilon_0}\frac{\varepsilon^s - \varepsilon_0}{2\varepsilon^s - \varepsilon_0} \quad \frac{\mu_0^2 - \mu_1^2}{R^3} \simeq \frac{1}{8\pi\varepsilon_0} \quad \frac{\mu_0^2 - \mu_1^2}{R^3} \tag{32}$$

for $\varepsilon^s \gg \varepsilon_0$, where μ_0 and μ_1 are the dipole moment of the charge distribution in the ground state and in the excited state respectively. For the dye 1AAQ the dipole moments have been evaluated according to semi-empirical method ZINDO/S: $\mu_0 = 1.4\,\text{Debye}$, $\mu_1 = 7.0\,\text{Debye}$. By using a radius $R = 4 \times 10^{-10}\,\text{m}$ evaluated on the basis of the molecular size of the dye, we obtain $\Delta V^{el} = -20\,\text{kJ/mol}$.

Let us consider the ratio between the dye photo-induced torque and the optical torque, which from Eqs. (1) and (30) can be written as

$$\frac{|\boldsymbol{\tau}_{dye}|}{|\boldsymbol{\tau}_{opt}|} = 2\frac{C_{dye}\Lambda}{k_e|\Delta\varepsilon^{opt}|}\left|\overline{D^2_{0,0}(\Omega)}\Delta V^{el}\right| \tag{33}$$

By considering the values of the molar absorption coefficients [7], one can estimates [5] the factor $C_{dye}\Lambda/\varepsilon_0 \approx 2.0 \times 10^7\,\text{J}^{-1}\,\text{s}^{-1}$ at the absorption wavelength $\lambda = 532$ nm and a dye fraction below 1%. Finally by assuming for the dye a typical order paramater $\overline{D^2_{0,0}(\Omega)} = 0.7$ and a decay rate $k_e \approx 10^{-9}\,\text{s}^{-1}$, and for the solvent an optical anisotropy $\Delta\varepsilon^{opt}/\varepsilon_0 = 0.7$ like for E7 [7], one obtains the following estimate

$$\frac{|\boldsymbol{\tau}_{dye}|}{|\boldsymbol{\tau}_{opt}|} \approx 800 \tag{34}$$

that is a reduction by a factor 30 of the threshold of the Freedericksz transition by dissolving the dye. Of course, a more precise evaluation would require an accurate determination of all these parameters. Still such an analysis shows that the predicted effect has the same order of magnitude found in the experiments [3,4].

To conclude we would like to point out the analogies and the differences with respect to previous theoretical treatments of the dye photo-induced effect [5,6]. We share with these analyses a common background provided by the diffusion model [17,18] for the rotational motion of the dye. On the other hand methodological differences emerge in relation to i) the mean field potential and to ii) the evaluation of the induced torque. In ref. [5,6] different interaction potentials are assumed for the ground state and the excited state, but without specifying the mechanisms responsible for them. On the contrary our analysis is based on the identification of them according to short range interactions and electrostatic interactions controlled by the solvent polarisation. Moreover in refs. [5,6] the induced torque is calculated through the difference on the rotational diffusion currents in the two states of the dye. We follow the alternative procedure of evaluating the free energy contribution due to dye-solvent interactions. Then, from its dependence on the director field, the dye photo-induced torque is derived in strict analogy to other torque contributions, for instance those due to elastic interactions [13]. Such a procedure is justified as long as a well defined time scale separation exists between the relaxation of molecular variables (orientation) and the relaxation of collective properties like the director field. We think that this is a convenient and general method which can be applied also to other models of dye-solvent interactions, for instance by including the effects of specific interactions like the formation of hydrogen bonds [8].

REFERENCES

[1] Elston, S. & Sambles, R. (1998). *The Optics of Thermotropic Liquid Crystals*, Taylor & Francis: London.
[2] Simoni, F. & Francescangeli, O. (1999). *J. Phys.: Condens. Matter*, *11*, R439.
[3] Janossy, I., Llloyd, A. D., & Wherrett, B. S. (1990). *Mol. Cryst. Liq. Cryst.*, *179*, 1.
[4] Janossy, I. & Llloyd, A. D. (1991). *Mol. Cryst. Liq. Cryst.*, *203*, 77.
[5] Janossy, I. (1994). *Phys. Rev. E*, *49*, 2957.
[6] Marucci, L. & Papparo, D. (1997). *Phys. Rev. E*, *56*, 1765.
[7] Marrucci, L., Paparo, D., Vetrano, M. R., Colicchio, M., Santamato, E., & Viscardi, G. (2000). *J. Chem. Phys.*, *113*, 10361.
[8] Marrucci, L., Paparo, D., Maddalena, P., Massera, E., Prudnikova, E., & Santamato, E. (1997). *J. Chem. Phys.*, *107*, 9783.
[9] di Matteo, A., Ferrarini, A., & Moro, G. J. (2000). *J. Phys. Chem. B*, *104*, 7764.
[10] di Matteo, A. & Ferrarini, A. (2001). *J. Phys. Chem. B*, *105*, 837.
[11] Stocchero, M., Ferrarini, A., & Moro, G. J. (2002). manuscript in preparation.
[12] Ericksen, J. L. (1966). *Phys. Fluids*, *9*, 1205.
[13] de Gennes, P. G. (1974). *The Physics of Liquid Crystals*, Clarendon Press: Oxford.
[14] Landau, L. & Lifchitz, E. (1969). *Éléctrodynamique des milieux continus*, MIR: Moscow.

[15] Rau, H. (1990). *Photochemistry and Photophysics*, CRC Press: Boca Raton, Chap. 4.
[16] Burnell, E. E. & de Lange, C. A. (1998). *Chem. Rev.*, *98*, 2359.
[17] Nordio, P. L. & Busolin, P. (1971). *J. Chem. Phys.*, *55*, 5485.
[18] Nordio, P. L., Rigatti, G., & Segre, U. (1972). *J. Chem. Phys.*, *56*, 2117.
[19] Rose, M. E. (1957). *Elementary Theory of Angular Momentum*, Wiley: New York.
[20] Bottcher, C. J. F. & Bordewijk, P. (1973). *Theory of Electric Polarization*, Elsevier: Amsterdam.