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Orientational dynamics of DR1 molecules in sol-gel films

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Abstract

A physical model for the induced orientation of azochromophores in sol-gel films is presented. This model describes the poling time dependence of the order parameter Φ based on a damped oscillator. This model provides a different approach to the chromophore orientational dynamics, with the property that all its parameters are physical meaningful. The model results have been experimentally verified in DR1 doped sol-gel films, by means of optical absorption measurements. We considered two kinds of sol-gel films: amorphous with a side-chain doping and mesostructured ones with a guest-host doping. The experimental results were fitted successfully with our model.

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1. Introduction

Functionalized polymers have been extensively studied to incorporate non-linear optical (NLO) chromophores into macromolecular systems. For an optimization of the second-order non-linear optical response in an assembly of NLO active molecules [1], a high degree of non-centrosymmetric order of the dipoles is needed. It can be attained by either electric field [2] or single-point Corona poling technique field [3]. In the last case an important goal is to get the alignment optimization of the dopant dipolar molecules under the influence of a d.c. external applied field. In order to do that, some studies have been performed to optimize the orientation by taking into account the intermolecular electrostatic [4–6] and the chromophore–matrix interactions [7,8]. Some models have been developed to describe the time dependence of this alignment [9,10] or even the time and temperature dependence of its relaxation [11].

In this work, we modeled the orientation dependence with respect to the poling time considering the equation of a damped oscillator. This model considers implicitly the chromophore-matrix interactions into the damping constant. We use this model to fit the behavior of the order parameter Φ as function of the poling time in different kinds of films. We analyzed the results previously obtained for two types of sol-gel materials, amorphous with a sidechain DR1 doping [12,13] and mesostructured with a guest-host DR1 doping [14]. The model predicts a minimum in the Φ parameter at short times and new experiments were performed to test this prediction with mesostructured films whose phase was controlled with carbazole [15].

In Section 2 we develop the model and describe the considerations that we did for applying it to the different kind of films. Section 3 contains the materials preparation and the experimental methods for poling the samples and for measuring Φ . The results are presented and discussed in Section 4. Finally, we give our conclusions in Section 5.

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2. Theory

2.1. Basics

In general, the planar structure of certain organic molecules, as azo-chromophores, is due to σ links, while the linear and non-linear optical properties of these molecules are mainly due to the π electrons involved in π links also present in their structure. The lateral overlapping of two carbon orbitals in a π link gives place to a mirror plane for the electron they share. This fact is the origin of the observed delocalization of the π electrons [16], which allows the traveling of the electrons along the entire molecule.

The optical absorption for a given organic molecule having an important dipolar moment may be expressed in terms of the component of the electric field of the light along the molecular dipole, $E_0 \sin \theta$, where E_0 is the magnitude of the electric field of the light and θ is the angle between the light propagation direction and the symmetry axis of the dipole ($\pi/2 - \theta$ is the angle between the light electric field and the dipole). We make this choice because we are interested in the angle between the applied poling field (Corona poling) and the axis of the molecule, which is, at normal incidence, the same angle between the light direction and the axis of the molecule. Finally, the poling field and the incident light have the same direction. Then, the light intensity absorbed by this molecule is proportional to the square of this component, $E_0^2 \sin^2 \theta$.

Since we are interested in the optical absorption of natural light by the sol-gel films, for each chromophore orientation there is a well defined angle between the chromophore main axis and some electric field component of the incident light.

For an azo-chromophore like disperse red one (DR1), which has a planar structure with a cylindrical symmetry and a large dipolar moment of 8.7 D [1], the π electrons are distributed as shown in Fig. 1. Fig. 1a allows to see that, when the entire molecule, and then its dipolar moment, is oriented parallel to the direction of the light (therefore perpendicular to the electric field of the light), there will be a very small light absorption cross section. In Fig. 1b is clear that a chromophore exhibits a maximum optical absorption when its dipolar moment is perpendicular to the direction of non-polarized light. Then, the optical absorption of one chromophore can be written as:

$$\alpha(\theta) = \alpha_{\rm m} \sin^2 \theta, \tag{1}$$

where α_m is the maximum optical absorption of one chromophore.

If we consider all the chromophores in a film then the total optical absorption (α_T) could be written as

$$\alpha_{\rm T}(\theta) = \alpha_{\rm m} \sum_{i=1}^{N} \, \sin^2 \theta, \tag{2}$$

where N is the total number of chromophores in the film.



Fig. 1. Electronic distribution of delocalized π -electrons for a DR1 azochromophore when the molecule is aligned (a) parallel and (b) perpendicular to incident light's direction.

Thus the average of the total optical absorption of the film is

$$A = \langle \alpha_{\rm T}(\theta) \rangle = \alpha_0 \langle \sin^2 \theta \rangle, \tag{3}$$

where we have defined the product $N\alpha_{\rm m}$ as the constant α_0 .

2.2. Damped oscillator

A permanent dipole under the influence of a constant electric field (as a Corona field is) behaves like an oscillator. For simplicity we consider each chromophore in the film subjected to a Corona field as an harmonic oscillator. The most general harmonic oscillator equation is

$$\ddot{\theta} + 2\gamma \dot{\theta} + \omega^2 \theta = F,\tag{4}$$

where dots are derivatives with respect to the poling time, θ is the angle between the dipole and the Corona field, γ is a damping constant, ω is the natural oscillation frequency of the dipole, and F is an external force (non-related to the Corona field). ω is related to the dipolar moment (μ) of the chromophore, the main inertia moment (I_{zz}) of the chromophore (due to the shape of DR1 molecule its main inertia moment is almost aligned to its dipolar moment), and the effective electric field inside the films, in the next way

$$\omega = \sqrt{\frac{\mu E}{I_{zz}}}.$$
(5)

The most general solution to Eq. (4) can be written as

$$\theta(t;\theta_0,\dot{\theta}_0) = \frac{F}{\omega^2} + \frac{\dot{\theta}_0 + \frac{(\theta_0\omega^2 - F)(\gamma + \Omega)}{\omega^2}}{2\Omega} e^{-(\gamma - \Omega)t} + \left(\theta_0 - \frac{F}{\omega^2} + \frac{-\dot{\theta}_0 + \frac{(F - \theta_0\omega^2)(\gamma + \Omega)}{\omega^2}}{2\Omega}\right) e^{-(\gamma + \Omega)t} \quad (6)$$

with θ_0 as the initial angular position of the chromophore, $\dot{\theta}_0$ its initial angular speed and $\Omega = \sqrt{\gamma^2 - \omega^2}$.

 γ represents the chromophore-matrix interactions, which avoid a fast chromophore orientation. *F* represents an effective force due to chromophore-chromophore interactions, which avoid a perfect alignment of the molecules along the Corona field direction.

2.3. Molecular angular distribution

The *N* chromophores of the sol-gel film are randomly oriented and they are homogeneously distributed before any Corona field is applied. With respect to the *z*-axis, which is perpendicular to the film surface, each chromophore can be oriented at an angle θ between 0 and 2π with equal probability.

Since there is azimuthall symmetry, the average of $\sin^2\theta$ over all the possible initial angular orientations is

$$\langle \sin^2 \theta(t;\theta_0,\dot{\theta}_0) \rangle_{\theta_0} = \frac{\int_{\theta_0=0}^{\theta_0=\pi} 2\pi \sin \theta_0 \sin^2 \theta(t;\theta_0,\dot{\theta}_0) \,\mathrm{d}\theta_0}{\int_{\theta_0=0}^{\theta_0=\pi} 2\pi \sin \theta_0 \,\mathrm{d}\theta_0}, \qquad (7)$$

with $\theta(t; \theta_0, \dot{\theta}_0)$ given by Eq. (6).

At t = 0 the system is in stationary equilibrium but the molecules may have an initial speed $\dot{\theta}_0$ different to zero. Assuming that all of their thermal energy corresponds to their rotational kinetic energy, then the molecules can have two most probable opposite initial speeds. They are given by

$$\dot{\theta}_0 = \pm \sqrt{\frac{k_{\rm B}T}{I_{zz}}},\tag{8}$$

where $k_{\rm B}$ is the Boltzmann constant and T the absolute temperature.

Because there are not great changes if we consider all the possible initial directions of movement, the complete average of $\sin^2\theta$ over the initial conditions can be written simply as

$$\langle \sin^2 \theta(t; \theta_0, \dot{\theta}_0) \rangle_{\theta_0, \dot{\theta}_0}$$

$$= \frac{\langle \sin^2 \theta(t; \theta_0, +\dot{\theta}_0) \rangle_{\theta_0} + \langle \sin^2 \theta(t; \theta_0, -\dot{\theta}_0) \rangle_{\theta_0}}{2}.$$
(9)

This complete average of $\sin^2 \theta$ depends explicitly on the poling time. This average is not exactly the same that the one expressed in Eq. (3), because thermal effects have not been considered yet (if we do not consider thermal effects, Eq. (3) would give us an absorbance tending to zero as the poling time get very large values, but such a thing has not been observed in this kind of materials). However Eq. (9) contains all the dynamics of the chromophores orientation. Employing Eq. (9) and incorporating thermal effects we will be able to describe how the optical absorption of a film changes with respect to the time of application of a Corona field at a given temperature *T*.

2.4. Thermal effects and the order parameter Φ

At every time chromophores are in movement due to thermal energy. This thermal movement avoids chromophores to acquire, during the poling process, a perfect orientation along the z-axis. The degree of orientation of the chromophores can be related to an order parameter Φ which considers the thermal energy contribution by means of a rigid oriented gas model [17]. This order parameter Φ is given by

$$\Phi(u) = 1 + \frac{3}{u^2} - \frac{3}{u} \coth(u),$$
(10)

with *u* the ratio of the electrostatic dipole alignment energy to the thermal energy

$$u = \frac{\mu E}{k_{\rm B}T}.$$
(11)

Here E is the same electric field than that one of Eq. (5).

The order parameter Φ describes the chromophore orientation when the film is at thermodynamical equilibrium. Which means that the statistical distribution $G(\theta)$ from which the expression of Φ is derived as in [17] is centered at $\theta = 0$

$$G(\theta) = e^{u\cos\theta}.$$
 (12)

Eq. (12) is only valid for a very large poling time, while the knowledge of an order parameter valid for all poling times requires to consider other kind of statistical distribution.

From Eq. (9) is possible to know, at any time, the orientation angle $(\bar{\theta})$ of a representative chromophore of the system

$$\bar{\theta}(t) = \arcsin\left(\sqrt{\langle \sin^2 \theta(t; \theta_0, \dot{\theta}_0) \rangle_{\theta_0, \dot{\theta}_0}}\right).$$
(13)

The angle $\bar{\theta}(t)$ depends on the poling time explicitly. In particular, the angle $\bar{\theta}(t)$ tends to zero when the poling time is very large. Thus, Eq. (12) is recovered at large poling times if we choose the next time-dependent statistical distribution for the system

$$G(\theta, t) = e^{u \cos(\theta + \bar{\theta}(t))}.$$
(14)

The main peak of this statistical distribution function is determined by $\bar{\theta}$, thus the main peak indicates the mean angular orientation of the chromophores in the films at each time. Besides, *u* determines how strong is the chromophores thermal agitation, i.e. the width of the statistical distribution function. In other words, Eq. (14) is the probability distribution function, at each time, of one chromophore, at temperature *T*, with an angular orientation equal to the mean angular orientation of all the chromophores in a film.

A time-dependent order parameter Φ can be deduced from the statistical distribution written in Eq. (14).

The order parameter of Eq. (10) has a direct experimental way to be measured by means of the optical absorption with normally incident natural light. The order parameter is related to the optical absorption as

$$\Phi(t) = 1 - \frac{A(t)}{A(t=0)}.$$
(15)

As a matter of fact Eq. (10) comes straightforward from Eqs. (12) and (15) for the steady state [17]. As can be seen from Eq. (3), the explicit expression for the order parameter requires the average of $\sin^2\theta$ which now is time depending and is given by

$$\langle \sin^2 \theta(t) \rangle = \frac{\int_{\theta=0}^{\theta=\pi} 2\pi \sin \theta [G(\theta, t) + G(-\theta, t)] \sin^2 \theta \, \mathrm{d}\theta}{\int_{\theta=0}^{\theta=\pi} 2\pi \sin \theta [G(\theta, t) + G(-\theta, t)] \, \mathrm{d}\theta}, \quad (16)$$

where the terms in the square brackets are the total distribution function of the system, which is always centered at the zero angle. Of course, the real total distribution function is not only centered at the zero angle, it also has its maximum value at the zero angle. We approximate the real distribution function with one which is centered at the zero angle, which have the same mean angular values than the real one, but steady-state at each poling time, in consequence, its maximum is not always at the zero angle and its shape is always the same. With Eqs. (15) and (16) we have a time-dependent order parameter, which is equal to that one of Eq. (10) for very large poling times.

3. Experimental

The sample preparation for the materials used in this work to test this model has been previously reported [12–15]. For the amorphous sol–gel films [12], the reorientable chromophore was disperse red 1 (DR1) functionalized in high concentration relative to the also functionalized molecule of carbazole (SiK) with a molar ratio of 1 DR1/5 carbazole/1 TEOS. These spin-coated samples had a thickness around of 1.3 μ m. An amorphous sol–gel film with sidechain DR1 doping, without carbazole and without HCl as a catalyzer was also considered [13].

For the mesostructured sol-gel films with a guest-host DR1-doping [14], the molar ratio was of 1 DR1/20 carbazole/20 SDS, where sodium dodecyl sulfate (SDS) is the ionic surfactant responsible of the lamellar phase structure of the material. These dip-coated films were withdrawn with a speed of 5 cm/min giving a thickness of 100 nm. Also, to test some of our model predictions, we prepared new mesostructured sol-gel films with guest-host DR1-doping, with the ionic surfactant cetyl trimethyl ammonium bromide (CTAB) and with different carbazole concentrations. We have reported that the molar ratio between carbazole and CTAB is the responsible of the hexagonal, mixed and lamellar phase structure of the material [15]. The ratios were 1 DR1/3 carbazole/10 CTAB, 1 DR1/4 carbazole/10 CTAB and 1 DR1/5 carbazole/10 CTAB for hexagonal, mixed and lamellar phases respectively. These dip-coated films were withdrawn with a speed of 5.3 cm/min giving a thickness of 100 nm.

The linear normal-incidence absorption was measured in amorphous sol-gel samples with carbazole and in mesostructured sol-gel samples with SDS, using a Milton Roy 5000 Diode Array spectrophotometer. The orientation of the DR1 molecules in the sol-gel film (and the non-linear optical properties of the material [9]) was induced by the single-point Corona poling technique (needle-surface distance = 12 mm, voltage = +6 kV d.c., poling temperature = 120 °C). The poling times studied for the amorphous samples were 10, 30, 60 and 120 min, while for the mesostructured were 6, 56 and 116 min. It is necessary to say that, for both cases, a new, different sample was used for each poling time studied. The absorption was measured before and after every poling process. In order to calculate the order parameter we considered the maximum absorption value of the DR1 main peak (at 490 nm wavelength).

For the amorphous sample without carbazole, as reported [13], the orientation was made by applying an external Corona field over the indium tin oxide (ITO) electrodes that are in contact with the sample. This orientation was estimated by measuring the order parameter by means of the ultraviolet–visible absorption spectra. We took the experimental data obtained by this group [13], to fit them by using our model.

For the new mesostructured samples prepared with CTAB and carbazole the linear normal-incidence absorption was measured using a ThermoSpectronic spectrophotometer model Genesys 2. In order to calculate the order parameter we considered the maximum absorption value of the DR1 main peak (at 490 nm wavelength). The orientation of the DR1 molecules in the sol–gel film was induced by the same single-point Corona poling described conditions.

4. Results and discussion

The experimental orientation dynamics for the mesostructured sol-gel samples with SDS and for the amorphous sol-gel samples are shown in Fig. 2. Each data set was fitted by using the following procedure. First, the maximum value of the order parameter is deduced by direct observation of the experimental results. This value allows us to find the magnitude of the electric field E, employing Eq. (10), and to solve it numerically. For solving Eq. (10) the following values were employed: $\mu = 2.871 \times 10^{-29} \text{ C m}$, $k_{\rm B} = 1.38 \times 10^{-23} \text{ J/K}$ and T = 393.15 K. Also, it is useful to consider the known value of the DR1 main inertia moment: $I_{zz} = 7.0 \times 10^{-43} \text{ kg m}^2$ [7] and with the obtained value for E and with Eq. (5), the ω value can be deduced. The calculation of the chromophores initial speeds from Eq. (8) requires using the I_{zz} value, too. Now it is possible to find an explicit expression for Eq. (9). We assume that the dipole-dipole electrostatic interactions are negligible (F=0) and we left γ as the unique fitting parameter.



Fig. 2. Experimental order parameter data showing the field-induced orientation as function of the poling time for (a) lamellar (SDS) [14], (b) amorphous (with carbazole) [12] and (c) amorphous (without carbazole) [13] sol–gel samples. The fitting curves are represented by continuous lines.

With a given γ (for simplicity we are only concerned with values such that $\gamma \gg \omega$, i.e., we consider the overdamped situation), from Eq. (13), it is possible to calculate the corresponding values of $\overline{\theta}(t)$ for each considered poling time. In consequence, there are as many statistical distributions $G(\theta, t)$ as considered poling times, and the same quantity of numerical integrations for obtaining $\langle \sin^2 \theta(t) \rangle$ has to be made. Each numerical integration gives a point in the plot $\Phi(t)$ in Figs. 2 and 3.

 $G(\theta, t)$ is obtained from Eq. (14), $\langle \sin^2 \theta(t) \rangle$ from Eq. (16), and the plots come directly from Eq. (15), with the calculated value $\langle \sin^2 \theta(t=0) \rangle = \frac{2}{3}$.

The fitting parameter γ values are shown in Table 1. As it can be observed in Fig. 2, our model predicts a minimum value for the order parameter Φ at very short times, where no data are reported. In order to test this prediction, we prepared the new mesostructured sol-gel films with CTAB and with different carbazole concentrations described above. The experimental orientation dynamics results for these three mesostructured phases of sol-gel samples with CTAB are shown in Fig. 3. Their fitting parameter values γ are also contained in Table 1. The data for the film with a lamellar structure confirm the negative Φ value prediction. We did not detect the minimum Φ value for the hexagonal structured film, maybe it is at shorter poling times. We did the detection of the minimum for the film with a mixed structure but it is not reliable at all, because of this kind of film exhibited a non-reversible damage of its optical properties, evident from the persistent loss of absorbance. However, we have fitted the data by means of Eq. (15) with an empirical extra term which represents an exponential degradation of the film. This equation is the following one:

$$\Phi(t) = 1 - \frac{A(t)}{A(t=0)} e^{-\lambda t},$$
(17)



Fig. 3. Experimental order parameter data showing the field-induced orientation as function of the poling time for (a) lamellar (CTAB), (b) mixed (CTAB) and (c) hexagonal (CTAB) structured sol-gel samples. The fitting curves are represented by continuous lines.

Table 1 Parameters used for the best fitting to the experimental results obtained for each studied material

Material	γ (s ⁻¹)	$arPhi_{ m max}$
Amorphous (with SiK) [12]	2.5×10^{24}	0.35
Amorphous [13] (without HCl as a catalyzer)	1.0×10^{25}	0.36
Lamellar (SDS) [14]	7.0×10^{24}	0.58
Lamellar (CTAB) [15]	5.0×10^{23}	0.39
Hexagonal (CTAB) [15]	1.8×10^{22}	0.39
Mixed (CTAB) [15]	-	-

where λ gives the degradation rate. The dotted line in Fig. 3b corresponds to a maximum order parameter Φ_{max} of 0.10, a γ value of $1.0 \times 10^{25} \text{ s}^{-1}$, and a λ value of $1.5 \times 10^{-2} \text{ s}^{-1}$.

By calculating the goodness of the fit [18], we found that the experimental results in all the fittings agree with the model with a precision bigger than 99.5%.

Fig. 4 relates the minimum in the order parameter function with the statistical distribution $G(\theta)$, i.e, relates the increase in the absorbance with the statistical distribution behavior. The existence of the minimum is due to the displacement of the maximum value of the statistical distribution $G(\theta)$ toward angles near to $\pi/2$ at very short times. Before any poling (t = 0) the statistical distribution is constant over all the θ angles. But the distribution moves toward larger angles when the corona field is turned on (from time t_1 until time t_2 in Fig. 4), due to the movement of the dipoles which initially are at larger angles than $\pi/2$ (the maximum value of the statistical distribution corresponds to the orientation angle $\overline{\theta}$ representative of all the



Fig. 4. Statistical distribution $G(\theta)$ vs. angle of orientation θ for different poling times. The figure corresponds to chromophores with initial angles in the range $[0,\pi]$. The $G(\theta)$ peak position represents the mean angular orientation of the chromophores, which always is in the range $[0,\pi]$. The $G(\theta)$ width is related to the chromophores thermal agitation. Thus, at very large times the $G(\theta)$ peak position is very near to zero and the thermal agitation determines the probability of the chromophores to be in other angles around the $G(\theta)$ peak position. By symmetry reasons, at each time the figure is similar for the chromophores with initial angles in the range $[-\pi, 0]$.

chromophores in the system, and is straightforward calculated from Eq. (13)). This movement gives place to the negative values of the order parameter Φ . For times larger than t_2 (in Fig. 4) the distribution returns to small θ values, and after a very large time (t_3 in Fig. 4) the distribution tends to be centered at zero.

As it can be seen in Figs. 2 and 3, the model proposed into this work fits well the observed response of the molecules to an external field for two different kinds of sol–gel materials, amorphous and mesostructured. This model has two main features, the first one is that all of its parameters are directly related to physical quantities of the system, the second one is that only one fitting parameter is required (if the maximum value for the order parameter is known).

We have two types of structures for the samples: mesostructured and amorphous. In the first one, due to the use of surfactant, the electrostatic interactions that oppose to chromophore orientation are different to that ones in the amorphous samples, in consequence the γ values in Table 1 are really different between the two kind of films. As a matter of fact, in general, the γ values for the amorphous samples are larger than or comparable to the γ values for the mesostructured films. Nevertheless, seeing the maximum value of Φ obtained for each case, we may say that there will be also a preferential orientation for the molecular dipoles when the surfactants induce a planar structure into the system.

We worked with two kinds of mesostructured films, classified by their surfactant: those which contain SDS and those which contain CTAB. It is remarkable that all the samples with CTAB exhibit shorter γ values than the rest of the samples.

As a matter of fact, there are molecules which modify the local electrostatic conditions of chromophores, and we have already shown for SiK that there is a change in the local electrostatic interactions [6]. The amorphous samples without carbazole have larger γ values than the amorphous samples with carbazole.

It is worthy to note that the γ values depend of two things: the kind of molecules which surround to the DR1 and the geometrical matrix structure. For instance, the sample without surfactants and without SiK has the largest values of γ , and the γ values for the films with a lamellar structure is at least one order of magnitude larger than the γ value for the film with an hexagonal phase structure.

5. Conclusions

A time-dependent model of the rotational response of dipolar molecules to an external applied electric field in amorphous and structured media has been proposed. This description has been verified experimentally by monitoring the optical absorption for amorphous and mesostructured sol-gel materials containing the reorientable dipolar chromophores DR1. A very good agreement between theory and experiment has been found, as a matter of fact, the negative values for the order parameter predicted by the model were observed experimentally. In opposition to a biexponential distribution model, the parameters involved into our model give information about the physical characteristics of the system, in which the chromophores are embedded. In particular, from the value of γ we obtained information about the electrostatic interactions existing into the system that oppose to chromophore orientation. Finally, we have shown from this analysis, that electrostatic damping can be modified for different sol–gel materials. In particular, the presence of carbazole and structure diminish this damping, which is an interesting feature that makes these materials more attractive for several applications.

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