Monte-Carlo simulation of the birefringence kinetics in azobenzene-containing materials

E Stoykova\textsuperscript{1,2,4}, G Mateev\textsuperscript{1}, B Blagoeva\textsuperscript{1}, L Nedelchev\textsuperscript{1,3} and D Nazarova\textsuperscript{1}

\textsuperscript{1}Acad. J. Malinowski Institute of Optical Materials and Technologies, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 109, 1113 Sofia, Bulgaria
\textsuperscript{2}VR/AR Research Center, Korea Electronics Technology Institute, 8 Floor, 11 World cup buk-ro 54-gil, Seoul, South Korea
\textsuperscript{3}University of Telecommunications and Post, 1 Acad. St. Mladenov, 1700 Sofia, Bulgaria

E-mail: estoykova@iomt.bas.bg

Abstract. The photoinduced optical anisotropy (birefringence and dichroism) in azobenzene-containing materials gives rise to a variety of applications in photonics by way of controlling the anisotropic properties at a nanoscale level. These applications require modeling the photoisomerization process kinetics. This is a complex and stochastic task that depends on many parameters. The paper presents a computationally effective Monte-Carlo simulation of recording, relaxation and erasure of the photoinduced anisotropy for a large number of 3D-oriented molecules at small angular increments between the neighboring orientations. The modeling is in good agreement with the experiment for measuring the birefringence in the PAZO polymer.

1. Introduction

The phenomenon of photoinduced optical anisotropy (POA) in azobenzene-containing materials, manifested as the appearance of birefringence and dichroism under irradiation with polarized light \cite{1}, finds various applications in photonics, optoelectronics and holographic data storage. Controlling the anisotropic properties at a nanoscale level is of vital importance for these applications and requires modeling the kinetics of the photo-reorientation of azochromophores during all typical processes occurring in the material, as e.g. recording, relaxation and erasure of birefringence \cite{2-4}.

The polarized light induces angular reorientation of the molecules via a sequence of reversible trans-cis-trans photoisomerization cycles. The trans isomers are axial molecules with a rod-like shape, so that the probability of their excitation depends on the angle between the polarization direction and the molecule dipole moment oriented along the long molecular axis. Thus, the governing mechanism of creating birefringence is the angular hole burning effect expressed as an excess of inactive azochromophores aligned perpendicularly to the pump light polarization direction. Alignment occurs through trans-cis-trans photoisomerization and remains preserved in its larger part after the end of the recording process.

Describing the kinetics of the angular reorientation of molecules while taking into account the spontaneous relaxation of the cis-state and thermal effects, such as rotational diffusion, is a complex task that depends on many parameters.
and stochastic in nature task characterized by many parameters. The Monte-Carlo method is a powerful approach for solving such a task due to its flexibility and the option for tracking the possible impact of any of the parameters involved [5,6]. The Monte-Carlo determination of the time-evolution of angular distributions of trans and cis isomers is based on a set of kinetic equations [2,7-10]. The statistical accuracy of the modeling depends on the number of processed molecules and a three-dimensional (3D) description of their orientations [1-14]. This fact entails using simplifications to decrease the computational burden of the simulation. Some solutions considered the problem as two-dimensional [7] and restricted the number of simulated orientations [7,11], excluded the thermal effects [11] or took a small number of molecules as a consequence of the limited power of the available computers [11,13].

This paper presents a Monte-Carlo simulation of recording, relaxation and erasure of the POA for a large number of 3D-oriented molecules at small angular increments between the neighboring orientations. We consider also the relaxation processes in which some of the reoriented trans molecules are randomized by thermal motion. The results are compared to an experiment performed using thin films of the azopolymer (poly[1-[4-(3-carboxy-4-hydroxyphenylazo) benzenesulfonamido]-1,2-ethanediyl, sodium salt]), shortly denoted as PAZO.

2. Description of the simulation approach

To simulate the photoinduced anisotropy kinetics, we estimated the signal at the output of an optical set-up consisting of two crossed polarizers and a thin film of an azobenzene-containing material placed between them [7]. In such an experiment, the power transmitted through the second polarizer is usually measured by a probe laser beam. The simulation includes three stages: i) recording stage under the action of linearly polarized light with a polarization direction at 45° to the transmission axis of the second polarizer by using a pump laser emitting in the absorption band of the azochromophore; ii) relaxation or reading stage, when the recording beam is turned off; iii) erasure stage under the action of a circularly polarized light or heating. The output signal is given by

\[ S(t) \propto N_t(\theta,t) \sin \left( 2\left( \theta - \frac{\pi}{4} \right) \right), \]

where \( N_t(\theta,t) \) is the number of trans molecules oriented at an angle \( \theta \) between the polarization direction and the transition dipole moment of the molecules at moment \( t \). As seen, the molecules aligned normally to the polarization axis of the pumping light give the main contribution into the signal.

We consider a photoisomerization cycle which includes the following steps: i) resonant excitation of a trans isomer followed by transition to the meta-stable ground state of the cis isomer; ii) resonant excitation of a cis isomer followed by transition to the trans ground state; iii) spontaneous relaxation of the metastable cis form to the stable trans form at a given lifetime of the cis state. The excited states of both trans and cis isomers are too short-lived with respect to the time scales of the POA kinetics to be taken into account. The photoisomerization and spontaneous relaxation are accompanied by reorientation of the molecules. The other reorientation mechanism is the thermally-induced rotational diffusion. The polarization direction of the pump light introduces symmetry in the model; the orientation of a molecule is given by \( \Omega = (\theta, \varphi) \) where \( \varphi \) is the azimuthal angle in the plane normal to the polarization direction.

Similarly to the previously reported models, our Monte-Carlo model follows the photoisomerization process as given at any moment \( t \) by the kinetic equations for the population densities \( \mathcal{T}(\Omega) \) and \( \mathcal{C}(\Omega) \) of trans and cis isomers with orientation \( \Omega = (\theta, \varphi) \) [10]:

\[ \frac{d\mathcal{T}(\Omega)}{dt} = -\eta \mathcal{P}_t(\Omega) + \eta' \mathcal{R}^\text{ct}(\Omega' \rightarrow \Omega) \mathcal{P}_c(\Omega') \mathcal{C}(\Omega') d\Omega' + \frac{1}{\tau_c} \left[ \mathcal{R}_c^\text{ct}(\Omega' \rightarrow \Omega) \mathcal{C}(\Omega') d\Omega' + \left( \frac{d\mathcal{T}(\Omega)}{dt} \right)_{\text{th}} \right], \]

(2)
\[
\frac{dC(\Omega)}{dt} = \eta I R_{tc}(\Omega') \rho_{t}(\Omega') R(\Omega') \kappa_{\Omega} - \eta P_{tc}(\Omega) C(\Omega) - \frac{1}{\tau_{c}} C(\Omega) + \left( \frac{dC(\Omega)}{dt} \right)_{sh},
\]

where \( P_{tc}(\Omega) \) and \( \eta, \eta' \) are the probabilities and quantum yields of \( \text{trans} \rightarrow \text{cis} \) and \( \text{cis} \rightarrow \text{trans} \) transitions, \( \tau_{c} \) is the lifetime of the \( \text{cis} \) state, \( R_{tc}, R_{ct}, R_{ct}^{c} \) are the probabilities for reorientation \( \Omega' \rightarrow \Omega \) at \( \text{cis} \rightarrow \text{trans} \) transition, \( \text{trans} \rightarrow \text{cis} \) transition and spontaneous relaxation of the \( \text{cis} \) state respectively. As mentioned in [10], equations (2) and (3) are written in a formal form in view of the fact that the \( \text{cis} \) configuration resembles more a spherical than an axial molecule. The last terms on the right-hand side of both equations give the kinetics of reorientation due to thermal diffusion. The excitation probabilities \( P_{t}(\Omega) \) differ for the three simulated stages as follows: i) \( P_{t}(\Omega) = \eta I \cos^{2}\theta \) and \( P_{c}(\Omega) = \eta I \) during the recording with \( I \) being the intensity of the pump light; ii) \( P_{t}(\Omega) = 0 \) and \( P_{c}(\Omega) = \eta I \) during relaxation at turning off the pump light; iii) \( P_{t}(\Omega) = \eta I_{\text{circ}} \) and \( P_{c}(\Omega) = \eta' I_{\text{circ}} \) during erasure with a circularly polarized light with intensity \( I_{\text{circ}} \). We assume uniform distribution of the probabilities \( R_{tc}, R_{ct}, R_{ct}^{c} \) with an option to introduce correlation between the new and the old molecule orientations.

In simulation, the quantities \( dT(\Omega) \) and \( dC(\Omega) \) were found at a single Monte-Carlo step, i.e. \( dt = 1 \).

At each step, we simulated all stochastic processes observed for the molecules in the \( \text{trans} \) and \( \text{cis} \) states according to their probabilities. A probability check was performed for each molecule, and a molecule involved in a \( \text{cis} \rightarrow \text{trans} \) transition was excluded from the spontaneous relaxation. To describe the 3D orientation of molecules, we represented the angular distributions \( T(\Omega) \) and \( C(\Omega) \) at a moment \( t \) as 2D arrays of size \( N_{\theta} \times N_{\phi} \) where \( N_{\phi} \) was the number of the simulated discrete values of the angle \( \theta \) and \( N_{\phi} \) was the number of \( \phi \) values. Thus, a single cell \((k,l)_{k=1..N_{\theta},l=1..N_{\phi}}\) in these arrays gives the number of \( \text{trans} \) or \( \text{cis} \) isomers oriented at \( \Omega = (\theta = k\Delta\theta, \phi = l\Delta\phi) \). A third dimension was added as \( T(k,l,n) = T(k\delta\theta,l\delta\phi,ndt) \) and \( C(k,l,n) = C(k\delta\theta,l\delta\phi,n\Delta t) \) to follow the photoisomerization process in time according to the scheme:

\[
T(k,l,n) = T(k,l,n-1) - DT(k,l) + RPC(k,l) + RSC(k,l),
\]

\[
C(k,l,n) = C(k,l,n-1) - DC(k,l) + RPT(k,l) - DSC(k,l),
\]

where \( n = 1..N \) indicates the current simulation step. The 2D arrays introduced in the right-hand side of equations (4) and (5) account for the reordering of the molecules orientations as readressing the molecule which has undergone a certain change of state and orientation as a result of transition or relaxation to a new cell. Accordingly, the \( DT \) and \( DC \) arrays give the number of molecules that have undergone \( \text{trans} \rightarrow \text{cis} \) and \( \text{cis} \rightarrow \text{trans} \) transitions; \( DSC \), the number of spontaneous relaxations of \( \text{cis} \) molecules; \( RPC \) and \( RSC \), the number of reoriented \( \text{trans} \) isomers at \( \text{cis} \rightarrow \text{trans} \) photoisomerization and spontaneous relaxation; \( RPT \), the number of reoriented \( \text{cis} \) isomers at \( \text{trans} \rightarrow \text{cis} \) photoisomerization. The randomizing effect of the rotational diffusion was simulated at substantial correlation between the new and old orientations. Usage of arrays allows for easy simulation of the reorientation by generating random integer numbers. As initial conditions, we assume that all molecules are in a \( \text{trans} \) state \( T \) and have an isotropic distribution.

3. Results and discussion

The algorithm developed was implemented as a MatLab code. Figure 1 shows the time evolution of the output signal \( S(t) \). The signal is given in arbitrary units. Initially, 50 molecules were added to each cell of the array \( T \) at \( t = 0 \) or \( n = 1 \). The angular increments were \( \Delta\theta = 2^{\circ} \) and \( \Delta\phi = 4^{\circ} \), so that \( T \) and \( C \) arrays were of size \( 91 \times 90 \) and contained a total of \( 409500 \) molecules. The lifetime of the \( \text{cis} \) state was 20 steps, \( \eta I = 0.2 \), \( \eta I = 0.4 \), \( \eta I = 0.03 \), \( \eta I = 0.06 \). The simulation was conducted for the case when the probability for excitation of the \( \text{cis} \) level is higher than that for the \( \text{trans} \) level. The curve obtained
corresponds to recording the photoinduced anisotropy from \( n = 1 \) to \( n = 600 \), to the relaxation process without illumination – from \( n = 601 \) to 1200, and to erasure from \( n = 1201 \) to 1400. The smoothness of the curve in figure 1 is due to the large number of processed molecules. The algorithm allows for observation of the angular distribution of the \( \text{trans} \) molecules at different moments. Four such distributions corresponding to the numbers in figure 1 are shown in figure 2, where figure 2 (a) reflects the early stage of recording when the \( \text{trans} \) isomers start grouping around the direction \( \theta = \pi/2 \); in figure 2 (b), the \( \text{trans} \) isomers are practically grouped around this direction. The relaxation process, when the orientations of \( \text{trans} \) isomers are slightly randomized due to spontaneous relaxation of the \( \text{cis} \) state and rotational diffusion, is shown in figure 2(c). The alignment of \( \text{trans} \) isomers normally to the polarization direction is destroyed under the action of circularly polarized light, as seen in figure 2(d).

**Figure 1.** Time evolution of the output signal at i) illumination with a linearly polarized light from \( n = 1 \) to 600 (recording), ii) turning off the light from \( n = 601 \) to 1200 (relaxation or reading), iii) illumination with a circularly polarized light from \( n = 1201 \) to 1400 (erasure); \( n \) is the number of Monte-Carlo steps. The numbers correspond to the distributions in figure 2.

**Figure 2.** Angular distributions of \( \text{trans} \) molecules at (a,b) recording, (c) relaxation and (d) erasure.

For optical testing, the PAZO polymer was dissolved in water and films were prepared by spin coating at 1500 rpm on glass substrates, thus forming 500-nm uniform thin films. The film thickness was measured by a high-precision Talystep profilometer (Taylor Hobson). To record and probe the photoinduced birefringence, two diode-pumped solid-state lasers were used: a recording laser with \( \lambda_{\text{rec}} = 444 \) nm, power of 35 mW; and a reading (probe) laser with \( \lambda_{\text{probe}} = 635 \) nm and power below
2 mW. The reading laser beam passed through a polarizer, oriented at 45°, while the recording beam passed through a vertical polarizer. After passing through the azopolymer sample, the reading beam entered a polarimeter (PAX5710 Polarization Analysing System, Thorlabs), which monitors the Stokes parameters of light in real time. In this case, the birefringence is given by the expression:

\[ \Delta n = \frac{\lambda_{\text{probe}}}{2nd} \arctan \left( \frac{S_2}{S_1} \right), \]  

where \( d \) is the film thickness, and \( S_2 \) and \( S_1 \) are the Stokes parameters \([15,16]\). During the recording, the light from the laser at 444 nm passed through a vertical polarizer, while for erasure, a quarter-wave plate was inserted in the beam path to produce circularly polarized light which randomized the orientation of the azochromophores and erased the birefringence. The result is shown in figure 3.

4. Conclusions
In summary, we proposed and implemented an algorithm for Monte-Carlo simulation of the photoinduced anisotropy kinetics in azobenzene containing materials under resonant excitation with a polarized light. The algorithm is computationally effective and allows one to include a large number of 3D oriented molecules at fine sampling of the orientations in space. The algorithm allows one to simulate recording, relaxation and erasure processes. The simulation result obtained for 409500 molecules oriented at 2° sampling of orientation in the plane passing through the polarization direction and the transition dipole moment of the \( \text{trans} \) molecules and 4°-sampling in the plane normal to the polarization direction are in good agreement with the birefringence curve measured in an experiment we performed with a PAZO polymer. Synthetic experiments with four times as many molecules and increased angular resolution were also performed.

Acknowledgements
The work was supported by the Bulgarian National Science Fund under project DN 08/10.

References
[1] Todoro T, Nikolova L, Stoilov G and Hristov B 2007 Appl. Opt. 46 6662
[2] Kiselev A 2002 J. Phys.: Cond. Matter. 14/49 13417-28
[3] Raschellà R, Marino I, Razzetti C, Bersani D and Lottici P 2007 JOSA B 24/3 504-9
[4] Toshchevikov V, Ilnytskyi J and Saphiannikova M 2017 J. Phys. Chem. Lett. 8/5 1094-98
[5] Cantatore V, Granucci G and Persico M 2012 J. Comput. Chem. 33/10 1015-22
[6] Batalla C 2008 Computer Methods in Appl. Mechanics and Eng. 197/41 3386-98
[7] Natansohn A, Rochon P, Gosselin J and Xie S 1992 Macromolecules 25/8 2268-73
[8] Dumont M, Sekkat Z, Loucif-Saibi R, Nakatani R and Delaire J 1993 Nonlinear Opt. 5 395
[9] Dumont M and Osman A 1999 Chem. Phys. 245/1 437-62
[10] Dumont M 2011 JOSA B 28/8 1855-65
[11] Pavlik G, Mitus A, Miniewicz A and Kajzar F 2003 J. Chem. Phys. 119/13 6789-6801.
[12] Pavlik G, Mitus A, Miniewicz A and Kajzar F 2004 J. Nonlinear Optical Phys. & Mater. 13/03 481-9
[13] Pawlik G, Kordas W, Mitus A, Sahraoui B, Czaplicki R and Kajzar F 2007 Optical materials in defence systems technology Proc. SPIE IV 674007
[14] Tavarone R, Charbonneau P and Stark H 2016 J. Chem. Phys. 144/10 104703
[15] Nedelchev L, Matharu A S, Hvilsted S and Ramanujam P S 2003 Appl. Opt. 42 5918
[16] Berberova N, Nazarova D, Nedelchev L, Blagoeva B, Kostadinova D, Marinova V and Stoykova E 2016 J. Phys.: Conf. Series 700 012032