

## MICROSCOPIC MODEL OF OPTICALLY INDUCED ANISOTROPY OF THIRD ORDER NONLINEARITY IN AZO-DYE POLYMER SYSTEMS

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The large photoinduced reversible change of third-harmonic generation in azo-dye polymer thin films has been recently observed. In present work, the microscopic interpretation of this phenomenon is given. The model presented is based on an angular hole burning and molecular reorientation due to *trans-cis* photoisomerization of azo-dye molecules.

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Optical phenomena related to the *trans-cis* photoisomerization of azo-benzene molecules are of stable interest because of potential applications in integrated optics and data storage devices [1]. It is well known that isomerization with respect to the  $-N=N-$  double bond results in quasi-permanent birefringence and dichroism [2]. The mechanism of the induced anisotropy can be summarized as follows. As the azo-dye molecule (e.g. disperse red 1 doped polymethylmethacrylate (DR1-PMMA)) in the *trans* form can be considered as a one-dimensional (rod-like) molecule, the probability of excitation by a linearly polarized light can be written as  $\text{Pr}(\theta_p) = \sigma_T I_p \cos^2 \theta_p$ , where  $\sigma_T$  is the cross-section for absorption of a photon by *trans* molecules parallel to the pump field and  $I_p$  is the pump intensity and  $\theta_p$  is the angle between the light-wave electric field and the molecular axis. This selective excitation leads to the angular hole burning (AHB) in the distribution of *trans* molecules, because after excitation the molecules tend to relax to the *cis* state with smaller polarizabilities. Reverse thermal *cis-trans* relaxation can go in two different ways: 1) to the original *trans* state; 2) to the *trans* state with a different orientation (Fig.1). If the molecule oriented along the pump polarization is excited, the relaxation in the second way reduces the probability of repeated excitation, therefore some molecular reorientation occurs. This molecular reorientation mechanism is important when *cis*-population is negligible (i.e. the pump intensity is low and if the thermal relaxation from *cis* to *trans* is fast).

The simplified AHB model [3] predicts an index variation (or an optical density variation) three times larger for a probe beam polarized along the polarization of pump beam than for a probe beam polarized perpendicularly ( $\Delta n_{||} = 3\Delta n_{\perp}$ ). However, the variation of the index observed experimentally is relatively small ( $\Delta n \sim 3 \cdot 10^{-3}$ ), so it can be detected only with very sensitive techniques, such as attenuated total reflection [1].

In this Letter, a microscopic model of photoinduced anisotropy of cubic nonlinear susceptibility in azo-doped polymer systems is presented. Contributions of the AHB and reorientation mechanisms are distinguished. Nonlinear optical properties of the molecular

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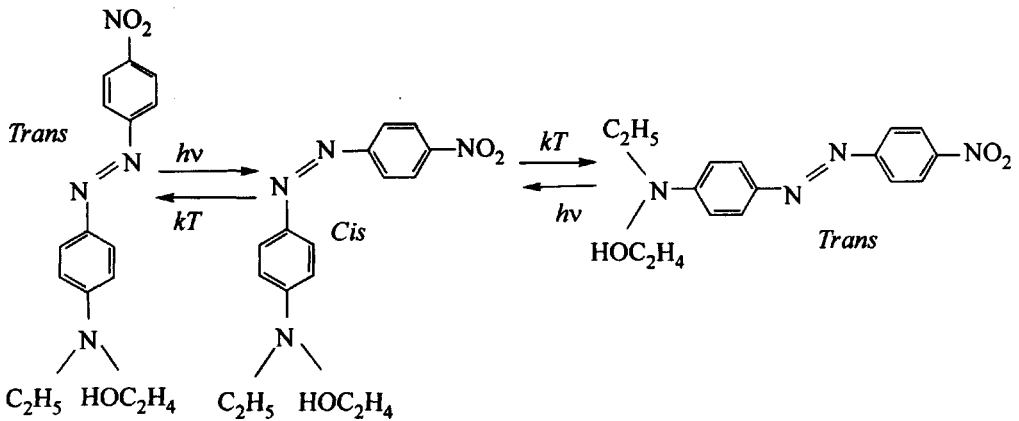


Fig.1. *Trans-cis* photoisomerization and reverse thermal *cis-trans* relaxation of DR1-PMMA molecule

distribution anisotropy are of interest because the general expression for second hyperpolarizability  $\gamma$  contains terms resonant for  $\omega$ ,  $2\omega$  and  $3\omega$  [4], so the third order effects are expected to be more sensitive to the change of the molecular conformation. Moreover, simple third-harmonic (TH) generation technique can be used to probe the induced anisotropy.

Several simplifying assumptions based on previous results are made in our model. First, a simple three-level model is applied (Fig.2). In fact, the reverse *cis-trans* photoi-

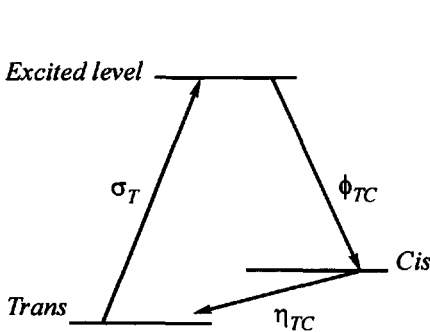


Fig.2. Simplified three-level scheme for *trans-cis* photoisomerization. Here  $\sigma_T$  is the cross-section for absorption of a photon by molecules parallel to the pump field,  $\phi_{TC}$  is the quantum yield for *trans* to *cis* transition and  $\eta_{CT}$  is the thermal relaxation rate from *cis* to *trans*

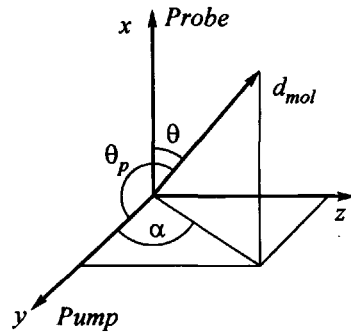


Fig.3. The diagram of molecular orientation with respect to the pump and probe electric fields. The pump and probe beams are polarized perpendicularly

somerization also exists, in competition with the direct *trans-cis* one, but can be neglected if the pump frequency is on the red side of *trans* absorption spectrum [2]. Second, third-order susceptibility of an azo-polymer is formed by only *trans* molecules (the contribution of the *cis* molecules and the polymer matrix is neglected). Third, molecular second hyperpolarizability of *trans* molecule has only one nonzero component  $\gamma = \gamma_{1111}$ , where the subscript means the direction of the molecular axis. The general expression for  $\chi^{(3)}$

responsible for TH generation by linearly polarized light will be then

$$\chi^{(3)}(-3\omega, \omega, \omega, \omega) = f^4 \gamma \int N_T(\Omega) \cos^4 \theta d\Omega \quad (1)$$

where  $f^4 = f_\omega^3 f_{3\omega}$  is a collection of the local field factors,  $N_T(\Omega)$  is a density of *trans* molecules oriented in the direction  $\Omega$ , and  $\theta$  is the angle between the probe beam electric field and the molecular direction  $\Omega$ . In the three-level model, the dynamics of *trans*-population is described by equation

$$dN_T(\Omega)/dt = -N_T(\Omega)\phi_{TC}Pr(\theta_p) + N_C(\Omega)\eta_{CT}, \quad (2)$$

where  $N_T(\Omega)$  and  $N_C(\Omega)$  are the densities of *trans* and *cis* molecules oriented in the direction  $\Omega$ ,  $Pr(\theta_p)$  is the probability of excitation of a *trans* molecule oriented at the angle  $\theta_p$ ,  $\phi_{TC}$  is the quantum yield for *trans* to *cis* transition and  $\eta_{CT}$  is the thermal relaxation rate from *cis* to *trans*. Taking into account the relation  $N_T(\Omega) + N_C(\Omega) = N/4\pi$ , where  $N$  is a density of *trans* molecules in original isotropic distribution, one can obtain the stationary angular molecular distribution

$$N_T(\Omega) = \frac{N}{4\pi}(1 + \phi_{TC}Pr(\theta_p)/\eta_{CT})^{-1}. \quad (3)$$

In the approximation of weak pump (i.e. far from the excitation saturation), the linear development of (3) gives

$$N_T(\Omega) = \frac{N}{4\pi}(1 - AI_p \cos^2 \theta_p). \quad (4)$$

In (4), we use the expression for  $Pr(\theta)$  and introduce  $A = \sigma_T \phi_{TC} / \eta_{CT}$ . If  $I_p = 0$ , the angular distribution of molecules is isotropic and

$$\chi_{iso}^{(3)} = \frac{1}{4\pi} f^4 \gamma N \int \cos^4 \theta d\Omega = \frac{1}{2} f^4 \gamma N \int_0^\pi \cos^4 \theta \sin \theta d\theta = \frac{1}{5} f^4 \gamma N. \quad (5)$$

This result is in agreement with Wong - Garito formula [5] applied to the case of random molecular orientation.

Now the  $\chi_{||}^{(3)}(-3\omega, \omega, \omega, \omega)$  responsible for TH generation by a probe beam polarized along the polarization of the pump beam is calculated. In this case  $\theta_p = \theta$  and one has

$$\chi_{||}^{(3)} = \frac{1}{2} f^4 \gamma N \int_0^\pi (1 - AI_p \cos^2 \theta) \cos^4 \theta \sin \theta d\theta = \chi_{iso}^{(3)} + \Delta\chi_{||}^{(3)} \quad (6)$$

with  $\Delta\chi_{||}^{(3)} = -\frac{1}{7} f^4 \gamma N AI_p$ . For a perpendicularly polarized probe beam  $\cos \theta_p = \sin \theta \cos \alpha$ , where  $\alpha$  is an azimuthal angle (Fig.3). Substituting this expression to (4) one has

$$\chi_{\perp}^{(3)} = \frac{1}{4\pi} f^4 \gamma N \int_0^{2\pi} \int_0^\pi (1 - AI_p \sin^2 \theta \cos^2 \alpha) \cos^4 \theta \sin \theta d\theta d\alpha = \chi_{iso}^{(3)} + \Delta\chi_{\perp}^{(3)} \quad (7)$$

with  $\Delta\chi_{\perp}^{(3)} = -\frac{1}{35} f^4 \gamma N AI_p$ . Therefore, one can see that  $\Delta\chi_{||}^{(3)} / \Delta\chi_{\perp}^{(3)} = 5$ . This result shows that the photoinduced anisotropy of  $\chi_{||}^{(3)}(-3\omega, \omega, \omega, \omega)$  due to the AHB mechanism is appreciably larger than that of the refractive index ( $\Delta n_{||} / \Delta n_{\perp} = 3$  [3]).

Another mechanism responsible for the optically induced anisotropy is angular redistribution of molecules. This mechanism has been widely developed to explain photoinduced birefringence and dichroism [6]. If the pump intensity is low enough, the *trans* molecules oriented near the pump polarization finally turn out near the plane perpendicular to the pump electric field vector. Therefore, in contrast to the AHB mechanism, the total number of *trans* molecules remains unchanged.

Let us suppose that there are  $N_{||}$  molecules with the orientation near the pump polarization. After reorientation, these molecules form isotropic angular distribution near the plane perpendicular to the pump electric field vector. Taking into consideration only  $N_{||}$  molecules, one has

$$\Delta\chi_{||}^{(3)} = -f^4\gamma N_{||}, \quad (8)$$

$$\Delta\chi_{\perp}^{(3)} = \frac{N_{||}}{2\pi} f^4\gamma N \int_0^{2\pi} \cos^4\theta d\theta = \frac{3}{8} f^4\gamma N_{||}. \quad (9)$$

Therefore, the angular redistribution mechanism gives a positive change of  $\chi^{(3)}$  for the probe beam polarized perpendicularly

$$\Delta\chi_{\perp}^{(3)} = -\frac{3}{8}\Delta\chi_{||}^{(3)}. \quad (10)$$

Eq.(10) shows that the angular redistribution of molecules can reduce the decrease of  $\chi_{\perp}^{(3)}$  caused by the AHB and, at low-intensity pump, even result in increase of  $\chi_{\perp}^{(3)}$ . It should be noted that the similar consideration for index gives the relationship  $\Delta n_{\perp} = -\Delta n_{||}/2$  (see, for example, [6]).

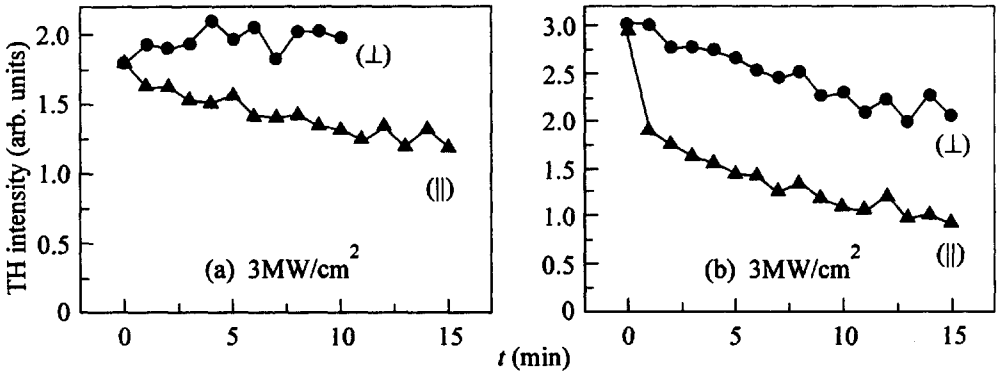


Fig.4. The TH signal in DR1-PMMA thin film pumped by 532 nm light as function of time. The pump intensities are 3 MW/cm<sup>2</sup> (a) and 30 MW/cm<sup>2</sup> (b). The pump is switched on at the moment  $t = 0$ . The TH is generated by the probe co-polarized (||) or cross-polarized ( $\perp$ ) with the fundamental frequency pump. The detailed description of the experimental setup can be found in [6]

Our recent experiments [7] have shown the remarkable decrease of TH generation in DR1-PMMA thin film pumped by the second harmonic of Nd:YAG laser. The TH generation decrease observed was too large to be explained by change of absorption due to *trans-cis* isomerization [8]. The change of the TH intensity was about 4 times for co-polarized pump and probe beams and only about 20 % for perpendicularly polarized beams. The decrease was almost completely reversible after few minutes of dark relaxation. Previous dichroism experiments [8] have shown that after the pumping beam is

switched off, the cis population responsible for AHB disappears in a few seconds, but the anisotropy due to the molecular re-orientation can survive several hours. Therefore, one can conclude that the  $\chi^{(3)}$  anisotropy studied in [7] is mainly due to the AHB mechanism. However, lately we observed an increase of the TH generated by the probe, which was polarized perpendicularly to the polarization of the low-intensity pump. Fig.4 demonstrates that, at low intensities, the reorientation mechanism dominates over the AHB mechanism, but the situation is quite reverse at high intensities. This observation along with the results of [7] can serve as an evidence of the model presented here. The large change of TH generation observed in [7] is of interest for applications such as optical memories, transient gratings, photonic band-gap devices, because it gives an opportunity of all-optical controlling third-order nonlinear properties of polymer materials.

In conclusion, the model presented predicts the third-order nonlinearity anisotropy in azo-dye polymer systems pumped by linearly polarized light. The model is in agreement with the results of recent experimental study of TH generation properties in azo-doped polymer thin films.

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