Polarization characteristics of nonlinear transmission in rigidly held saturable-dye molecules with random orientations

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Abstract. Polarization-dependent nonlinear transmissions are investigated by a pump-probe method in saturable-dye-doped films in which optically anisotropic saturable dyes are rigidly held with random orientations. The nonlinear transmissions measured by using uranine-doped poly(vinyl alcohol) films are compared with the theoretical predictions that are obtained by considering the effects of pump propagation and molecular orientation on the basis of a rate equation analysis for a four-energy-level model including an excited-state absorption. The measurements were conducted for the two cases of polarization states for which the polarization direction of the probe wave is either parallel or perpendicular to that of the pump wave; the experimental results considerably deviated from the theoretical ones for the probe wave perpendicularly polarized to the pump wave. It is shown that this is explained by modifying the energy level model to include the existence of a nearly-orthogonal component of the transition dipole moment associated with the ground-state absorption in uranine dyes.

1. Introduction

Saturable-dye-doped solid films have been widely used as a phase conjugator chiefly because of their relatively low saturation intensity and easy preparation of large samples in area; their possible applications for real-time image processing have also been demonstrated [1,2]. In dye-doped films, optically anisotropic dye molecules are fixed in solid polymer matrix with random positions and orientations, being isotropic as a whole. Irradiated with linearly polarized intense light, the dye molecules whose transition dipole moments are near directed to the polarization direction are selectively excited and highly saturated by the incident wave. This leads to photo-induced uniaxial anisotropy whose optic axis is defined by the polarization direction. Thus, the nonlinear polarization induced in such films depends not only on the light intensity but also on the polarization states of incident light waves, leading to polarization-dependent saturable absorption characteristics as shown by Kramer et al. [3]. The polarization characteristics of nonlinear transmissions in those media were revealed by Montecchi et al. [4] by comparing the experimental results with the theoretical ones based on a four-energy-level model for the saturable dyes. In our measurements on the nonlinear transmissions by a pump-probe method in uranine-doped poly(vinyl alcohol) (PVA) films, however, the experimental results considerably deviated from the theoretical ones for the case of the probe wave perpendicularly polarized to the pump wave. We investigate a possible mechanism for this observation, in this work, and show that these deviations from the theoretical predictions are explained by the existence of a nearly-orthogonal component of the transition dipole moment associated with the ground-state absorption in uranine dyes.
2. Theory
2.1. Molecular orientation of saturable dyes and Energy-level model
Saturable dyes are basically modeled by a four-energy-level system including an excited-state absorption [4,5], and nonlinear polarization in this system can be derived from a rate equation analysis. In references [4] and [5], the directions of the transition dipole moments associated with a ground- and an excited-state absorption are assumed to be parallel to each other, and each dye molecule is assumed to have only one component of the transition dipole moment associated with the ground-state absorption [6]. In this work, however, we modify the energy-level model to include a nearly orthogonal component of that associated with the ground-state absorption. Thus, we define the directions of the transition dipole moments associated with each absorptive transition in a laboratory coordinate system as shown in figure 1.

In figure 1, \(e_\mu\) stands for the unit vector along the transition dipole moments associated with the ground- and the excited-state absorption, and \(e_u\) the nearly orthogonal component of that associated with the ground-state one, which is assumed to be at an angle \(\beta\) from \(e_\mu\) in a molecular coordinate system. In the present model, the \(e_u\) component is assumed not to contribute to the changes in the population densities among the energy levels. The pump wave is assumed to be linearly polarized along the x-direction, and the probe wave to be either parallel or perpendicularly polarized to the pump wave.

Figure 2. Energy level diagram for saturable dyes as a five level system including the nearly orthogonal component of the ground-state absorption as well as the excited-state absorption. \(\sigma_0\), \(\sigma_1\) and \(\sigma_T\) are the absorption cross sections associated with each absorptive transition, \(\tau_f\) and \(\tau\) are a fluorescent and a phosphorescent life time, and \(\gamma\), \(\gamma_1\) and \(\gamma_T\) are the transition rates associated with an inter-system crossing for \(\gamma\) and internal conversions for \(\gamma_1\) and \(\gamma_T\), respectively.
Thus, the saturable dyes are modeled by a five energy-level system including the nearly orthogonal component of the ground-state absorption as well as the excited-state absorption, as shown in figure 2. In figure 2, levels 1, 2 and 2’ are singlet states, while levels 3 and 4 triplet states. The molecule excited by the incident light from its ground state, level 1, occupies the lowest excited-triplet state, level 3, with certain probability through intersystem crossing, since the triplet state has relatively long phosphorescent lifetime. Thus, the depletion of the ground-state population density gives rise to the saturable absorption effect. \( \sigma_0 \) and \( \sigma_T \) stand for the absorption cross sections associated with the ground- and the excited-state absorption, respectively, which cause the depletion of the ground-state population density. On the other hand, \( \sigma_1 \) represents the nearly orthogonal component of that associated with the ground-state absorption, which is assumed not to contribute to the changes in the population densities among the energy levels. \( \tau_f \) and \( \tau \) are a fluorescent and a phosphorescent lifetime, respectively. \( \gamma \) denotes the transition rate for an intersystem crossing, while \( \gamma_1 \) and \( \gamma_T \) the ones for internal conversions. As mentioned in figure 1, in this model, the transition dipole moments associated with \( \sigma_0 \) and \( \sigma_T \) are assumed to be parallel each other, having the \( e_\mu \) direction, and the one associated with \( \sigma_1 \), having the \( e_u \) direction, is nearly orthogonal to them.

2.2. Rate equation analysis for nonlinear transmission

The population density of each level can be derived from the rate equation analysis. In this model, the appreciably populated states are only the ground and the lowest triplet state, levels 1 and 3. The steady-state population densities of these levels are obtained as [5,7]

\[
\rho_1 = \frac{1}{1 + R_0^2 I_0 / I_{SAT}}, \quad \rho_3 = 1 - \rho_1 = \frac{R_0^2 I_0 / I_{SAT}}{1 + R_0^2 I_0 / I_{SAT}}, \quad R_0 = e_\mu \cdot e_0, \quad (1)
\]

where \( \rho_1 \) and \( \rho_3 \) are the population densities of the ground and the excited state, respectively, \( I_0 \) is the intensity of the pump wave, and \( e_0 \) stands for the unit vector along the polarization direction of the pump wave. Here, the changes in the population densities are influenced by the \( e_\mu \) component of the transition dipole moment alone, and the effects of the molecular orientation are accounted for by the term \( R_0 \). In equation (1), with the frequency \( \nu \) of the incident light and Plank’s constant \( h \), a saturation parameter \( I_{SAT} \) is defined as

\[
I_{SAT} = \frac{h \nu}{\sigma_0 q \tau}, \quad q = \frac{\gamma}{1/\tau_1 + \gamma}. \quad (2)
\]

Here, \( q \) is triplet yield, which represents the quantum yield of triplet formation.

The nonlinear absorption properties can be derived from the results of the rate equation analysis. The saturated absorption cross section of each dye molecule for the probe wave polarized to an \( e_{Pr} \) direction is obtained as

\[
\sigma = e_\mu R_0^p (\sigma_0 \rho_1 + \sigma_T \rho_3) + e_0 R_0^p \sigma_1 \rho_1, \quad R_0^p = e_\mu \cdot e_{Pr}, \quad R_1^p = e_\mu \cdot e_{Pr}. \quad (3)
\]

In the case of the pump wave linearly polarized to the \( x \)-direction (\( e_0 = e_x \)), the scalar products of the unit vectors are given by

\[
R_0 = R_0^p = \cos \theta, \quad R_1^p = \cos \theta \cos \beta - \sin \theta \cos \chi \sin \beta \quad (4)
\]

for the parallel polarized probe wave (\( e_{Pr} = e_x \)), and

\[
R_0^p = \sin \theta \sin \phi, \quad R_1^p = \sin \theta \sin \phi \cos \beta + (\cos \theta \sin \phi \sin \chi + \cos \phi \cos \chi) \sin \beta \quad (5)
\]

for the perpendicularly polarized probe wave (\( e_{Pr} = e_y \)). The nonlinear absorption coefficient \( \alpha \) is obtained by taking orientational average of \( \sigma \) as
Here, \( N \) is the number density of the dye molecules, and the bracket denotes orientational averaging.

The nonlinear transmission for each polarization state can be obtained by the following procedures. The pump propagation effect is, first, revealed by numerically solving the nonlinear propagation equation for the pump intensity \( I_0 \) as a function of \( z \), penetration depth in the dye-doped film, together with equations (1)-(4) and (6):

\[
\frac{dI_0}{dz} = -\alpha_S(I_0)I_0.
\] (7)

Then, the nonlinear transmissions for the probe wave parallel (\( T_S \)) and perpendicularly (\( T_P \)) polarized to the pump wave can be calculated from the nonlinear propagation equations for the probe intensity \( I_p \) with film thickness \( L \):

\[
\frac{dI_p}{dz} = -\alpha_S(I_0)I_p, \quad T_S = \frac{I_p(L)}{I_p(0)},
\] (8)

by using equation (4) for the parallel polarized probe wave;

\[
\frac{dI_p}{dz} = -\alpha_P(I_0)I_p, \quad T_P = \frac{I_p(L)}{I_p(0)},
\] (9)

by using equation (5) for the perpendicularly polarized probe wave. In the propagation equations, the nonlinear absorption coefficients for the parallel (\( \alpha_S \)) and the perpendicularly (\( \alpha_P \)) polarized probe wave are given by

\[
\alpha_S(I_0) = \alpha \cdot e_x = N(\sigma \cdot e_x), \quad \alpha_P(I_0) = \alpha \cdot e_y = N(\sigma \cdot e_y),
\] (10)

respectively, as a function of the pump intensity \( I_0 \). In this system, as a result of the random orientation of the dye molecules, a small-signal and a large-signal absorption coefficient are given as

\[
\alpha_0 = \alpha_S(0) = N(\sigma_0 + \sigma_1)/3, \quad \alpha_\infty = \alpha_S(\infty) = N\sigma_1/3,
\] (11)

respectively, and saturation intensity \( I_S \) is defined by [5]

\[
\alpha_S(I_S) = (\alpha_0 + \alpha_\infty)/2.
\] (12)

Here, \( I_S \) differs numerically from \( I_{SAT} \) of equation (2) by a constant factor.

2.3. Numerical results

Figure 3 shows the numerical results of the nonlinear transmission as a function of the pump intensity \( I_0 \) normalized by the saturation intensity \( I_S \) for the probe wave parallel (\( T_S \) in the figure) and perpendicularly (\( T_P \) in the figure) polarized to the pump wave. The solid lines stand for the nonlinear transmissions obtained by considering the effects of the nearly orthogonal component of the absorption cross section \( \sigma_1 \) associated with the ground-state absorption, and the dashed lines those obtained by ignoring the effects of \( \sigma_1 \). In the numerical calculations, the angle \( \beta \) is assumed, for simplicity, to be 90 degrees, and the following parameters are used: the product of the small-signal absorption coefficient \( \alpha_0 \) and the film thickness \( L \) as \( \alpha_0L=1.0 \); the ratios of absorption cross sections as \( G_0=\sigma_0/\sigma_0=0.46 \) and \( G_1=\sigma_1/\sigma_0=0.15 \) for the solid lines, and as \( G_0=0.40 \) and \( G_1=0 \) (\( \sigma_1=0 \)) for the dashed lines.

The effects of the absorption cross section \( \sigma_1 \) are clearly seen in figure 3. While the parallel component \( T_S \) is decreased in the region of relatively high pump intensity, the perpendicular one \( T_P \) is...
increased within the wide range of the pump intensity. This can be attributed to the effects of the direction of the transition dipole moment associated with $\sigma_1$. The dye molecule closely oriented to the polarization direction of the linearly polarized pump wave highly occupies its excited state with the irradiation of the pump wave; this leads to the simultaneous extinctions of the absorptive transitions associated with $\sigma_0$ and $\sigma_1$. On the other hand, the dye molecule perpendicularly oriented to the polarization direction of the pump wave remains in its ground state up to considerably high pump intensity. As a result, the nonlinear transmissions, $T_S$ and $T_P$, are changed by the way observed in figure 3.

Figure 3. Nonlinear transmission $T$ as a function of the pump intensity $I_0$ normalized by the saturation intensity $I_s$ for the probe wave parallel ($T_S$) and perpendicularly ($T_P$) polarized to the pump wave. The solid and the dashed lines are the corresponding theoretical curves calculated with (solid lines) and without (dashed lines) considering the effects of the nearly orthogonal component of the absorption cross section $\sigma_1$ associated with the ground-state absorption.

3. Experimental results and discussion
In the experiment, uranine-doped PVA films with the thickness $L$ of about 80 $\mu$m were used as the saturable absorbing media. A strong pump and a weak probe wave from an Ar-ion laser were adjusted to overlap incoherently in the dye-doped film to suppress any wave-mixing processes. The probe intensity was set to be 1/100 as large as the saturation intensity to avoid additional saturation. The polarization direction of the linearly polarized probe wave was at 45 degrees to that of the linearly polarized pump wave. After passing through an interference filter to eliminate fluorescence and phosphorescence emitted from the dye-doped film, the transmitted probe wave was divided into two components that are parallel and perpendicularly polarized to the pump wave by a Wollaston prism. Each polarization component was detected by a photo-diode, from which the nonlinear transmission for the parallel component $T_S$ and for the perpendicular component $T_P$ was derived. The measurements were conducted at the wavelength of 514.5 nm.

Figures 4(a) and 4(b) show the experimental results of the pump-intensity dependence of the nonlinear transmission measured by using the uranine-doped PVA film with $\alpha_0L$ of 0.50. The symbols are the experimental data for $T_S$ (closed circles) and for $T_P$ (closed triangles), and the solid lines are the corresponding theoretical curves obtained (a) by ignoring the effects of the nearly orthogonal $e_0$ component of the absorption cross section $\sigma_1$ associated with the ground-state absorption, and (b) by considering these effects. The parameters of $I_s$, $G_0$, and $G_1$ determined by least-square curve fitting are listed in each figure. It is found from figure 4 that, while the experimental data for the perpendicular components $T_P$ deviate considerably from the theoretical curve without considering the effects of $\sigma_1$ in (a), they agree quite well with that obtained by considering these effects in (b). These tendencies were reproducibly observed in the various samples having the different values of $\alpha_0L$. 


Similar deviations of the experimental data from the theoretical curve for the perpendicular component $T_P$ seen in figure 4(a) were also observed in the results shown in reference [4].

![Graph](image)

**Figure 4.** Experimental results of the pump-intensity dependence of the nonlinear transmission measured by using the uranine-doped PVA film with $\alpha_0L$ of 0.50. The closed circles are the experimental data for $T_S$ and the closed triangles for $T_P$, and the solid lines are the corresponding theoretical curves. The effects of the nearly orthogonal component of the absorption cross section $\sigma_1$ associated with the ground-state absorption are ignored in the calculations of (a), while considered in the calculations of (b).

Figures 5 and 6 show the experimental results of the pump-intensity dependence of the nonlinear transmission measured by using the uranine-doped PVA film with $\alpha_0L$ of 1.02 in figures 5(a) and 5(b), and of 2.13 in figures 6(a) and 6(b). As in figure 4, the experimental data for the perpendicular components $T_P$ agree quite well with the theoretical curve obtained by considering the effects of $\sigma_1$ in (b). When the direction of the transition dipole moment associated with the excited-state absorption cross section $\sigma_T$ inclines from that associated with the ground-state one $\sigma_0$, the theoretical curves of the nonlinear transmissions, $T_S$ and $T_P$, are also changed by the angle between the dipole moments associated with $\sigma_0$ and $\sigma_T$ [7]. The numerical calculations, however, revealed that the theoretical curves obtained by considering this effect decreases $T_P$ contrary to the experimental results.

![Graph](image)

**Figure 5.** Experimental results of the pump-intensity dependence of the nonlinear transmission measured by using the uranine-doped PVA film with $\alpha_0L$ of 1.02. The meanings of the symbols and the lines are the same as those in figure 4. The effects of the absorption cross section $\sigma_1$ are ignored in the calculations of (a), while considered in the calculations of (b).
Figure 6. Experimental results of the pump-intensity dependence of the nonlinear transmission measured by using the uranine-doped PVA film with $\alpha_0 L$ of 2.13. The meanings of the symbols and the lines are the same as those in figure 4. The effects of the absorption cross section $\sigma_1$ are ignored in the calculations of (a), while considered in the calculations of (b).

The saturable absorption parameters of $I_S$, $G_0$ and $G_1$ determined by the least-square curve fitting in (b) of figures 4-6 are listed in table 1. Reproducibility of the determination of these parameters was examined by using the samples with $\alpha_0 L$ being approximately equal to 1.0. The mean values with standard deviations among twelve measurements were 0.40 with 0.07 for $I_S$ in W/cm², 0.30 with 0.05 for $G_0$, and 0.21 with 0.03 for $G_1$, respectively. Although the scattering of data is slightly large, the obtained parameters are consistent with each other among three values of $\alpha_0 L$.

| $\alpha_0 L$ | $I_S$ [W/cm²] | $G_0$ | $G_1$ |
|-------------|---------------|-------|-------|
| 0.50        | 0.50          | 0.25  | 0.22  |
| 1.02        | 0.34          | 0.28  | 0.22  |
| 2.13        | 0.34          | 0.31  | 0.18  |

4. Conclusions
In this work, the polarization-dependent nonlinear transmissions were investigated by the pump-probe method in the saturable-dye-doped films in which optically anisotropic saturable dyes are rigidly held with random orientations. The nonlinear transmissions measured by using the uranine-doped PVA films were compared with the theoretical predictions obtained by considering the effects of the pump propagation and the molecular orientation on the basis of the rate equation analysis. For the saturable dyes, the four-energy-level model with the excited-state absorption previously used was extended, in this work, to include the nearly orthogonal component of the absorption cross section $\sigma_1$ associated with the ground-state absorption, which is assumed not to contribute to the changes in the population densities among the energy levels. The measurements were conducted for the two cases of polarization states for which the polarization direction of the probe wave is either parallel or perpendicular to that of the pump wave. The experimental data considerably deviated from the theoretical prediction for the case of the probe wave perpendicularly polarized to the pump wave.
without considering the effects of the absorption cross section $\sigma_1$; it was found, however, that this discrepancy becomes significantly small by considering the effects of $\sigma_1$. These tendencies were reproducibly confirmed in the various samples with the different values of $\alpha_0L$ at the wavelength of 514.5 nm from the Ar-ion laser. In the analysis of the polarization characteristics of wave mixing processes, such as phase conjugation and two-wave mixing, in the materials consisting of saturable-dye molecules rigidly held with random orientations, it is important to include the effects of the nearly orthogonal component shown in this work.

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