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MEASUREMENTS OF NONLINEAR ABSORPTION IN AZO DYE DOPED LIQUIDS

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We present a simple experimental method for the determination of several parameters characterizing the photisomerization of an azo dye dopant in a liquid host. A combination of intensity-dependent transmission measurements and the relaxation of the transmission after illumination yields the sought-after parameters. These parameters are needed for a quantitative analysis of light-induced birefringence and dichroism within the framework of a dynamical mean-field model.

Keywords: azo dyes; Jánossy-Effect; nonlinear absorption

INTRODUCTION

In the last decade there has been considerable interest in azo dye doped materials. They have applications in the fields of optical information processing and optical data storage due to their unique properties owing to photoisomerization of the azo group [1]. Nevertheless, the underlying mechanisms are still not fully understood. The central question is the role of the azo dye in processes of light-induced anisotropy and molecular reorientation. Several investigations were carried out on azo dye doped nematics [2,3] and azo-polymers [4,5]. However, in both types of materials the interpretation of measurements can be a difficult task. In nematics, possible photoalignment processes at the sample surfaces in combination with the elastic orientational coupling, as well as the collective behaviour of the molecules can hinder a exhaustive clarification of the mechanisms. In polymers, the azo groups are attached to the polymer backbone as side chains and the dynamics are very slow. Since the described drawbacks do not play a role in azo dye doped liquids, they pose an interesting alternative for the investigation of photoinduced orientational mechanisms. Moreover,

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they have the isotropy in common with the polymers and fast dynamics like nematics. New insights from investigations of azo dye doped liquids can help understand the processes in the other material classes as well.

Similar as in the case of anthraquinone dye doped liquids [6], the orientational dynamics and the photoinduced transitions in azo dye doped liquids can be described in the framework of a mean-field model. The model provides rate equations for the number densities and order parameters of the host and of the involved electronic and isomeric states of the dye dopant. From these equations, the dynamics of anisotropic optical quantities, like birefringence and dichroism, can be deduced. The aim of this paper is to provide measurements of the parameters in the model, which characterize the absorption and photoisomerization of a specific dye dopant. The knowledge of these parameters is necessary for a quantitative comparison of the full dynamical model with experimental data on light-induced birefringence and dichroism. The full dynamical model and its comparison with experiments will, however, be published elsewhere.

THEORETICAL DESCRIPTION

A theoretical expression for the time- and intensity dependent absorption of an azo dye doped liquid for a cw light beam is derived in this chapter. Later, we use this theoretical expression in a least squares fitting procedure to experimental data, which yields the parameters of our interest as fit-parameters.

We model the photoisomerization of the azo dye with the simplified scheme sketched in Figure 1. Two major simplifications of the photoisomerization process are made: First, we consider a single reaction coordinate, which may be the bend or the torsional angle of the benzene rings around the central double bond of the azo group; the exact intramolecular mechanism of photoisomerization is not important here and hence not further specified. Second, we assume a single excited state common to the trans and cis isomeric forms. In reality, photoisomerization may proceed along paths on a multidimensional energy hypersurface, which are different for trans $\rightarrow$ cis and cis $\rightarrow$ trans transitions [1]. In our model, the photoexcitation from the trans or cis ground state to the excited state is followed by a fast (< 1 ps) relaxation to the minimum of the excited state. Subsequently, the molecules relax within several 10 ps to the ground state [7]. On this relaxation, the molecule can either proceed to the trans ground state with probability Φ_t or to cis with probability Φ_c. Hence,

$$\Phi_c + \Phi_t = 1. \tag{1}$$

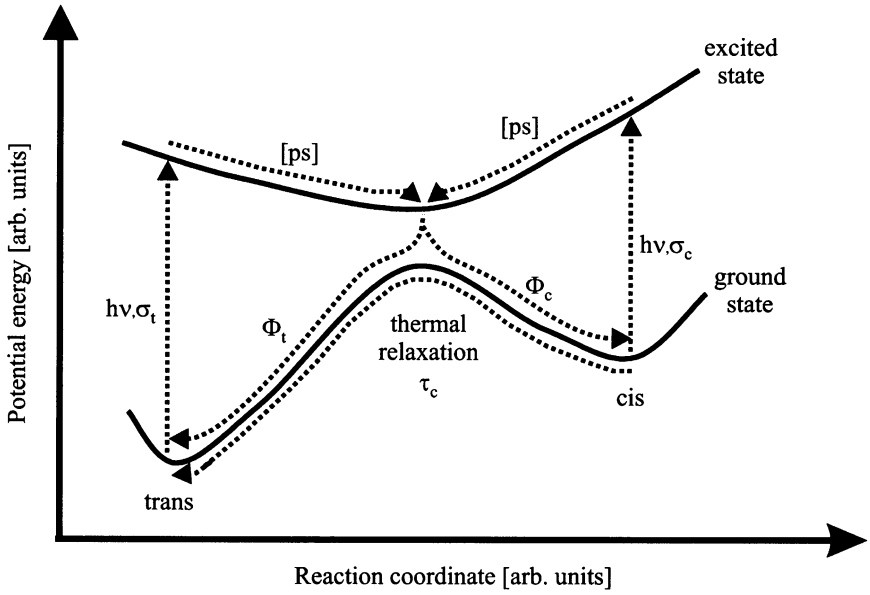

FIGURE 1 Simplified isomerization scheme of azo dyes.

The rate equations for the number density of the cis state N_c can be written as:

$$\frac{dN_c}{dt} = -\frac{N_c}{\tau_c} + \alpha_t \frac{I}{h\nu}\Phi_c - \alpha_c \frac{I}{h\nu}\Phi_t. \tag{2}$$

The first term describes the thermal relaxation from cis to trans. The second term accounts for the photoinduced transitions from the trans to cis state, and the last term for the photoinduced cis to trans transitions. τ_c is the lifetime of the cis isomer in darkness, $\alpha_{c/t}$ are the absorption coefficients of cis and trans isomers, h is the Planck-number, ν the frequency and I the intensity of the light beam.

The overall dye number density $N_d = N_c + N_t$ is conserved, i.e., $N_d \equiv$ const. In our measurements, we use moderate cw-intensities, such that there is no considerable orientational order induced. Hence, the trans and cis order parameters are zero and for the absorption coefficients follows:

$$\alpha_{c/t} = \frac{\sigma_{c/t} N_{c/t}}{3}, \tag{3}$$

with $\sigma_{c/t}$ as the absorption cross sections of trans and cis, respectively. Using Eqs. (1) and (3), the cw solution (I $\equiv$ const.) of Eq. (2) is:

$$N_c = N_c^0 e^{-kt} + N_c^{stat}\left(1 - e^{-kt}\right), \tag{4}$$

with k as the decay rate of cis isomers under illumination and N_c^{stat} as the steady-state number density ($t \to \infty$) [8]:

$$k = \frac{1}{\tau_c} + \frac{I}{3h\nu}(\sigma_t \Phi_c + \sigma_c \Phi_t), \quad N_c^{stat} = \frac{N_d \sigma_t \Phi_c}{\frac{3h\nu}{I\tau_c} + \sigma_t \Phi_c + \sigma_c \Phi_t}. \tag{5}$$

From Eqs. (3) and (4), the overall absorption coefficient

$$\alpha = \alpha_t + \alpha_c, \tag{6}$$

of the dye doped liquid can be deduced. By measuring the relaxation of α after illumination, the cis lifetime in darkness, τ_c, can be determined. Intensity-dependent transmission measurements yield the parameters σ_t, σ_c and Φ_t.

EXPERIMENTAL SETUP

In this chapter, a description of the investigated sample and of the experimental setup is given.

The sample consists of a 300 µm thick cuvette, filled with a solution of 0.1 wt.-% R4, a bis-azo dye, dissolved in 5CB. The molecular structures can be found in [9]. All measurements were carried out at 38°C, where the mixture is in the isotropic phase.

The measurements of absorption and relaxation can be made with the simple setup sketched in Figure 2. In this setup, a frequency-doubled Nd:YAG cw-laser emits a linearly polarized beam at $\lambda = 532$ nm. The beam passes through an acousto-optical modulator and pinhole for intensity control. A small amount is coupled out with a glass wedge behind the pinhole for monitoring the input intensity with photodiode PD1. To reduce the disturbing influence of interferences from multiple reflections at the sample windows, the laser traverses the sample convergently. The sample is placed in a temperature-controlled oven ($\Delta T \approx 0.1$ K). Lens L3 guides the beam

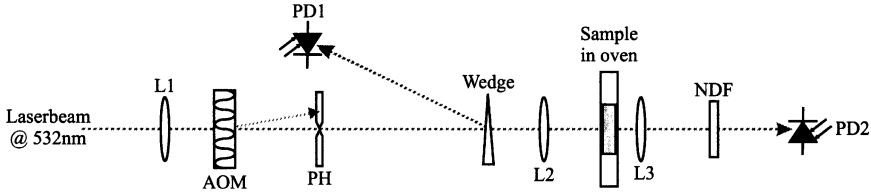

FIGURE 2 Setup for measurements of nonlinear absorption and its relaxation. PD: photodiodes, L: lenses, PH: pinhole, AOM: acousto-optical modulator, NDF: neutral density filter.

through a neutral density filter (NDF) onto photodiode PD2, which measures the power transmitted through the sample.

ABSORPTION MEASUREMENTS

The intensity is tuned stepwise from low to high values. In each step, the intensity is set and held for 5 seconds to prevent transient effects during the measurement. Then a computer records the transmitted power before the next intensity-step is made. In order to be sensitive to the absorption of the dye only, the measurements with the dye doped sample are normalized to those with a reference sample, filled only with the pure 5CB host. The absorption is then determined by:

$$\alpha = -\frac{1}{L}\ln\left(\frac{T_{\text{doped}}}{T_{\text{ref}}}\right), \tag{7}$$

with L as the sample thickness and $T_{\text{doped/ref}}$ as the transmittances of dye doped and reference sample. In order to exploit the optimum dynamic range of the photodiodes, several measurements were carried out at different intensity ranges. These measurements are shown together with the theoretical curve in Figure 3. The main error source for the slight scattering of the absolute absorbance, especially between the different intensity ranges, is that the dye doped and reference sample must be exchanged between the acquisitions and thus the reflection losses vary slightly.

RELAXATION MEASUREMENTS

For the relaxation measurements, we first set the intensity to its maximum of $4300\,\text{W/m}^2$ for longer than 40 seconds. This ensures that a stationary trans-cis equilibrium is established. After this "pumping", the intensity is set to $0.5\,\text{W/m}^2$, which is too low to influence the decay of the trans-cis ratio considerably. With a digital storage oscilloscope, the power transmitted through the sample is recorded with a time resolution of 100 ms. The final data shown in Figure 4 is an average over more than 20 repetitions of the acquisition procedure.

RESULTS AND DISCUSSION

In order to determine the parameters σ_t, σ_c, Φ_t and τ_c, we perform a least-square fitting procedure simultaneously on the two acquired data sets, i.e., to the intensity-dependence and to the relaxation of the absorption.

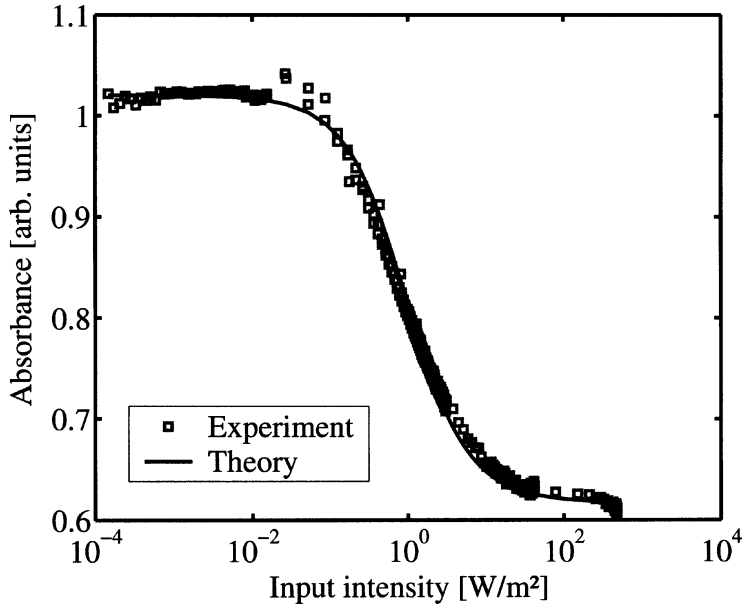

FIGURE 3 Absorbance of the dye in the sample versus input intensity. A semi-logarithmic plot is used to visualize details at low intensities. The absorbance in the low intensity limit depends only on σ_t. The high intensity limit is determined by a combination of Φ_t, σ_t and σ_c. All four parameters σ_t, σ_c, Φ_t and τ_c together characterize the position and shape of the turning point in the absorbance-graph.

Instead of directly using Eq. (6) for the absorption, we also take into account that the intensity inside the sample decreases along the propagation direction z of the beam due to intensity-dependent absorption. For this purpose, we divide the sample into 150 thin slices in our calculations. In each of these slices, the intensity and such the absorption coefficient can be considered as constant along z. When changing from 100 to 150 slices, there is no significant change in the results, so the division is fine enough.

For the fitting procedure, equal weights are assigned to both measurements. By changing the weights from 1:1 to 9:1 and 1:9, the results change by less than 1 per mill. This shows that both measurements deliver a consistent set of values for the parameters.

The resulting best-fit values of the parameters are:

$$\begin{array}{cc} \sigma_t = 6,4 \cdot 10^{-21}\, m^2, & \sigma_c = 7,2 \cdot 10^{-22}\, m^2, \\ \Phi_t = 92\%, & \tau_c = 21,5\, s. \end{array} \tag{8}$$

As it can be expected from similar measurements in the nematic phase at slightly shorter wavelengths [8], the absorption cross section is larger for

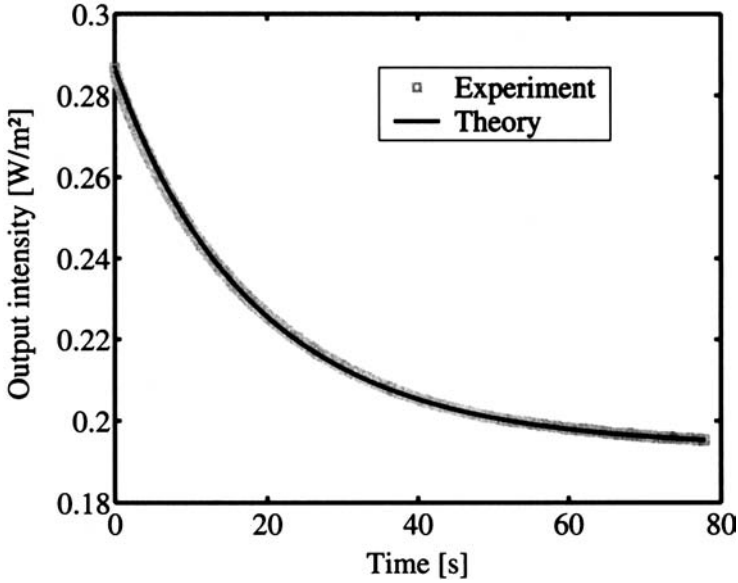

FIGURE 4 Relaxation of transmission through sample (input intensity before the relaxation: $4300\,W/m^2$, input intensity during relaxation: $0.5\,W/m^2$). The shape of the curve is strongly sensitive to the cis-life-time τ_c.

the trans isomer than for the cis isomer. Moreover, we find that a large fraction of the molecules goes to the trans isomer on relaxation from the excited state. The cis lifetime found in our measurements is about a factor of two larger than the one found by Jánossy *et al.* for the same dye [8]. However, they used a different host (E63 from Merck) and measured in the nematic phase at room temperature. It has been shown that the cis lifetime can strongly depend on temperature [10], which might explain the observed deviation. Further investigations are under way to clarify the dependence of the cis lifetime on the host, the temperature and on the thermodynamic phase.

CONCLUSIONS

The simplified isomerization scheme is a sufficient description of the photoisomerization of the R4 azo dye despite the assumption that there is only a single reaction coordinate and a single excited state common to both trans and cis isomers. For the determination of the parameters in the simplified isomerization model, straightforward transmission measurements can be used. The independence of the best-fit parameters regarding

the weights assigned to the different measurements supports the reliability of the values. The cis lifetime determined in our measurements is about twice as high as the value reported in [8] for the same dye, which has been measured under different conditions. For a clarification of the dependence on these conditions, further experiments have to be carried out. Our main result is the quantitative determination of the parameters characterizing the photoisomerization of the azo dye dopant in the isotropic phase. These parameters will be used in a detailed analysis of induced birefringence and dichroism in the isotropic phase of R4 azo dye doped 5CB.

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