PHOTOINDUCED DICHROISM AND VIBRONIC RELAXATION OF RHODAMINE DYES

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The absorption anisotropy of rhodamine dye molecules in various solvents is measured on a picosecond time scale. The dye solutions are partially bleached with pump pulses and the dichroism is measured with delayed perpendicularly polarized probe pulses. The experimental results are compared with the linear oscillator model.

The absorption spectra of dye solutions measured with conventional spectral photometers are independent of the polarization of the incident light. The solutions show isotropic behavior since all molecular orientations have the same probability. Absorption anisotropy is observed for dyes embedded in stretched foils [1] and for dye solutions that are subjected to hydrodynamic [2] or electric fields [3]. The acting forces partially orient the molecules. The dichroism indicates that the dye molecules have different absorption cross sections $\sigma_\parallel$ and $\sigma_\perp$ for light polarized parallel and perpendicular to the molecular axis, respectively. Since the orientation of the molecules is not complete [4] the measured dichroism $D = (\alpha_\parallel - \alpha_\perp)/(\alpha_\parallel + \alpha_\perp)$ gives only a qualitative indication of the molecular dichroism $D_m = (\sigma_\parallel - \sigma_\perp)/(\sigma_\parallel + \sigma_\perp)$. $\alpha_\parallel$ and $\alpha_\perp$ indicate the absorption coefficients for light polarized parallel and perpendicular to the orienting direction. The anisotropy of dye molecules was studied extensively by measuring the degree of polarization of fluorescence light [5–8]. In most cases the molecules were excited by linear polarized light and the polarization $P = (I_\parallel - I_\perp)/(I_\parallel + I_\perp)$ of the fluorescence light emitted under 90° to the propagation direction of the exciting light was measured. $I_\parallel$ and $I_\perp$ are the components of the fluorescence light polarized parallel and perpendicular to the polarization of the exciting light. The dye molecules with their transition moments parallel to the polarization direction of the exciting light are preferentially excited. An anisotropic distribution of the excited mole-

cules results that is monitored by observing the degree of polarization of the fluorescence light. Only dyes dissolved in highly viscous solvents can be investigated by this technique since otherwise rotational reorientation within the fluorescence decay time disturbs the induced anisotropy. The concentration of the dissolved dyes has to be kept very low ($\lesssim 10^{-5}$ M/ℓ) to eliminate energy transfer from the excited molecules to (differently oriented) unexcited molecules within the fluorescence lifetime.

The light absorption of the dyes is caused by electric dipole transitions. A classical description of the absorption process leads to the linear oscillator model [5]. This model predicts a molecular dichroism of $D_m = 1$ and a fluorescence polarization of $P = 0.5$ for $S_0 - S_1$ transitions in dyes. The measured dichroism for dyed films was found to be $D \lesssim 0.8$. The molecules are not completely aligned so that no conclusion about the true value of $D_m$ can be drawn. The limiting values of fluorescence polarization (called fundamental polarization) in highly viscous solvents at very low concentrations are found to be $P_0 \lesssim 0.46$. They do not reach the theoretical value of $P_0 = 0.5$ (for a discussion see below).

In this letter we describe a new technique for the investigation of molecular dichroism. An intense picosecond light pulse bleaches the dye partially and generates an anisotropic orientation of the molecules. A weak probe beam polarized perpendicular to the strong exciting pulse monitors the absorption anisotropy.

Additionally to the determination of the dichroism this method allows within a certain time range to measure the vibronic relaxation $\tau$ of the excited molecules by scanning the probe beam through a delay range of a few tens of picoseconds. The rotational redistribution lies in the range between 200 ps and several nanoseconds for our solutions [9] and does not disturb the determination of $D_m$ and $\tau$. The molecular dichroism can be measured for dyes in any solvent. Higher dye concentrations can be used in our experiments than for the fluorescence polarization technique, since the concentration dependent energy transfer to unexcited molecules is negligible on a picosecond time scale.

We determined the absorption anisotropy of rhodamine dyes in several solvents. We restricted our measurements to the determination of the dichroism of the $S_0$–$S_1$ transition at a fixed frequency. The described technique can be extended to the measurement of dichroitic spectra by applying an intense monochromatic picosecond pump pulse and a weak picosecond probing continuum [10].

The absorption of polarized light by dye molecules depends on the angle $\theta$ between the direction of the electrical dipole transition moment and the direction of the polarization vector of the light wave. The absorption cross section for an ideal linear oscillator is given by $\sigma(\theta) = \sigma \cos^2\theta$. The conventionally measured absorption cross section for dye solutions is obtained by integration over all orientations of the isotropically distributed molecules

$$\sigma_M = \int \sigma(\theta)\, d\Omega / \int d\Omega = \int_0^{\pi/2} \sigma \cos^2\theta \sin\theta\, d\theta = \sigma/3 .$$

For a linear oscillator it is $\sigma_\parallel = \sigma$, $\sigma_\perp = 0$ and $D_m = 1$. In our measurements we want to determine $D_m$. We allow $\sigma_\perp \neq 0$ in our calculations and use the ansatz $\sigma(\theta) = \sigma_\parallel \cos^2\theta + \sigma_\perp \sin^2\theta$ (see below). For this situation the conventional transmission measurement leads to $\sigma_M = \frac{1}{3}(\sigma_\parallel + 2\sigma_\perp)$. For $\sigma_\parallel \neq \sigma_\perp$ the pump pulse induces an anisotropy to the orientational distribution of the molecules remaining in the ground state. The absorption of the probe beam polarized perpendicular to the pump beam depends on the ratio $\sigma_\perp/\sigma_\parallel$ and therefore on $D_m$.

To describe the absorption processes we have to introduce a model for the relevant transitions in our spe-

cial case. A five-level system gives a rather realistic picture of our dyes (see ref. [11]). The laser light excites the molecules from the ground state $S_0$ to a Franck–Condon state in the first excited singlet state $S_1$. The molecules decay from the Franck–Condon state to a temporary equilibrium position in the $S_1$ state with a time constant $\tau$. From the first excited singlet state $S_1$ absorption of laser light to higher lying singlet states is taken into account by an excited state absorption cross section $\sigma_{ex}$. For the excited state absorption we assume the same branching ratio $\sigma_{\perp ex}/\sigma_{\parallel ex}$ as in the ground state (fluorescence polarization spectra indicate the same orientation of the transition moments [1]). The fluorescence relaxation of molecules in $S_1$ state to a Franck–Condon level in the $S_0$ state occurs in the nanosecond range and does not affect the picosecond measurements. Light propagation through the dye is determined by the following equations:

$$\partial I_L/\partial z + (n/c)\, \partial I_L/\partial t$$

$$= -\frac{2}{\pi} \int_0^{\pi/2} \int_0^{\pi/2} \{A(\theta)[N_1(\theta,\phi) - N_2(\theta,\phi)] $$

$$+ A_{ex}(\theta)[N - N_1(\theta,\phi)]\} \sin\theta\, d\theta\, d\phi , \tag{1}$$

$$\partial I_P/\partial z + (n/c)\, \partial I_P/\partial t$$

$$= -\frac{2}{\pi} \int_0^{\pi/2} \int_0^{\pi/2} \{B(\theta,\phi)[N_1(\theta,\phi) - N_2(\theta,\phi)]$$

$$+ B_{ex}(\theta,\phi)[N - N_1(\theta,\phi)]\} \sin\theta\, d\theta\, d\phi , \tag{2}$$

$$\partial N_1(\theta,\phi)/\partial t = -(1/h\nu_L)[A(\theta)I_L + B(\theta,\phi)I_P]$$

$$\times [N_1(\theta,\phi) - N_2(\theta,\phi)] - [N_1(\theta,\phi) - \bar{N}_1]/\tau_{or} , \tag{3}$$

$$\partial N_2(\theta,\phi)/\partial t = (1/h\nu_L)\{[A(\theta)I_L + B(\theta,\phi)I_P]$$

$$\times [N_1(\theta,\phi) - N_2(\theta,\phi)]$$

$$- [A_{ex}(\theta)I_L + B_{ex}(\theta,\phi)I_P]N_2(\theta,\phi)\}$$

$$- N_2(\theta,\phi)/\tau - [N_2(\theta,\phi) - \bar{N}_2]/\tau_{or} . \tag{4}$$

The initial conditions are

$$I_L(t, r, z = 0) = I_{0L} \exp[-(t/t_0)^2 - (r/r_0)^2] , \qquad (5)$$

$$I_P(t, r, z = 0) = I_{0P} \exp\{-[(t-t_D)/t_0]^2 - (r/r_0)^2\} , \qquad (6)$$

$$N_1(t-nz/c = -\infty, r, z, \theta, \phi) = N , \qquad (7)$$

$$N_2(t-nz/c = -\infty, r, z, \theta, \phi) = 0 . \qquad (8)$$

The following abbreviations are used in eqs. (1)–(4):

$$A(\theta) = \sigma_\| \cos^2\theta + \sigma_\perp \sin^2\theta ,$$

$$A_{ex}(\theta) = \sigma_{\|ex} \cos^2\theta + \sigma_{\perp ex} \sin^2\theta ,$$

$$B(\theta, \phi) = \sigma_\| \sin^2\theta \cos^2\phi + \sigma_\perp (1 - \sin^2\theta \cos^2\phi) ,$$

$$B_{ex}(\theta, \phi) = \sigma_{\|ex} \sin^2\theta \cos^2\phi + \sigma_{\perp ex} (1 - \sin^2\theta \cos^2\phi) ,$$

$$\bar{N}_1 = \frac{2}{\pi} \int_0^{\pi/2} \int_0^{\pi/2} N_1(\theta, \phi) \sin\theta \, d\theta \, d\phi ,$$

$$\bar{N}_2 = \frac{2}{\pi} \int_0^{\pi/2} \int_0^{\pi/2} N_2(\theta, \phi) \sin\theta \, d\theta \, d\phi .$$

$I_{0L}$ and $I_{0P}$ are the peak intensities of the incident picosecond pump pulse and the perpendicularly polarized probe pulse, respectively. The temporal and spatial shape of the pulses is assumed to be gaussian. $2t_0$ and $r_0$ are the $1/e$ values of the pulse duration and the beam radius. $t_D$ is the delay time between pump beam and probe beam. $\nu_L$ is the frequency of the laser pulses (both pulses have the same frequency). $n$ is the refractive index of the dye solution. $N$ is the total number density of dye molecules. $N_1(\theta, \phi)$ and $N_2(\theta, \phi)$ describe the density of molecules in the ground state and the excited Franck–Condon state, respectively. $\theta$ is the angle between the transition moment of the molecule and the polarization of the pump pulse. $\phi$ is the azimuthal angle of the transition moment relative to the polarization of the probe pulse. The orientational redistribution of the molecules by rotational brownian motion is taken into account in a phenomenological manner by the last terms of eqs. (3) and (4). At large delay times the rotational redistribution increases the transmission of the probe beam. The transformation $z' = z$ and $t' = t - nz/c$ brings the equation system to a simpler form. Solutions for the trans-

mitted intensities $I_L(t', r, z' = l)$ and $I_P(t', r, z' = l)$ are obtained by numerical methods. The energy transmissions of the pump pulse $T_L$ and the probe pulse $T_\perp$ are calculated by integrating the transmitted intensities over space and time and by dividing through the input energies.

The energy transmissions $T_L$ and $T_\perp$ are determined by the system parameters $N$, $\sigma_\|$, $\sigma_\perp$, $\sigma_{\|ex}$, $\sigma_{\perp ex}$, $\tau$ and $\tau_{or}$, the pulse parameters $I_{0L}$, $I_{0P}$, and $t_0$ and the delay time $t_D$. $N$ is given by the dye concentration. The absorption parameters $\sigma_\|$, $\sigma_\perp$, $\sigma_{\|ex}$ and $\sigma_{\perp ex}$ can be expressed by the parameters $\sigma_M = (\sigma_\| + 2\sigma_\perp)/3$, $\sigma_{ex,M} = (\sigma_{\|ex} + 2\sigma_{\perp ex})/3$, and $D_m = (\sigma_\| - \sigma_\perp)/(\sigma_\| + \sigma_\perp) \approx (\sigma_{\|ex} - \sigma_{\perp ex})/(\sigma_{\|ex} + \sigma_{\perp ex})$. $\sigma_M$ is obtained by absorption measurements at the frequency $\nu_L$ with a spectral photometer. The $\sigma_{ex}$ values were determined by energy transmission measurements of the pump beam at high intensities in ref. [11]. $D_m$ will be determined in this letter by measuring the energy transmission ratio $T_\perp/T_L$ and by comparison with calculated curves. $\tau$ has been determined with two different techniques in ref. [11]. In this letter an upper limit of $\tau$ can be determined from the dependence of $T_\perp/T_L$ on the delay time $t_D$ at fixed peak intensities $I_{0L}$ and $I_{0P}$.

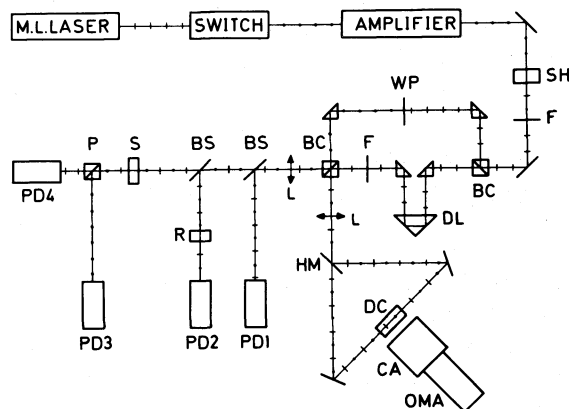The experimental set-up is depicted in fig. 1.



Fig. 1. Experimental set-up for the measurement of dichroism. SH, ADP crystal for second harmonic generation; F, filters; BC, beam dividing cubes; WP, $\lambda/2$ waveplate; DL, variable delay line; L, lenses; HM, 50% mirror; DC, two-photon fluorescing dye for pulse duration measurement; CA, camera; OMA, optical multi-channel analyzer system; BS, beam splitters; R, rutile crystal for intensity determination; S, sample; P, polarizer; PD1-4, photodetectors. Light polarization is indicated by —+— and —•—.

A mode-locked Nd-glass laser [12] was used for the generation of trains of picosecond light pulses. An electro-optical shutter selects a single pulse from the beginning of the pulse train and a subsequent Nd-glass amplifier increases the energy of the pulse to approximately 3 mJ. The light pulses ($\lambda = 1.06 \ \mu m$) have a duration of $\Delta t \approx 5$ ps (fwhm) and a bandwidth of $\Delta \tilde{\nu} \approx 3 \ cm^{-1}$ (fwhm). Using an ADP crystal the pulses are frequency doubled with a conversion efficiency of $\approx 20\%$. The fundamental light pulse is absorbed by the filter F following the ADP crystal. Two green light pulses are generated with the help of a 50% beam dividing cube. One pulse travels through a delay line and is reduced in intensity by a factor of 16 with an appropriate filter F. This pulse serves as the probe pulse. The other pulse acts as intense pump pulse. Its polarization is rotated by 90° with a $\lambda/2$ wave plate. Part of the pulse energy is used for the determination of the pulse duration in a two-photon fluorescence system. 9,10-diphenylanthracene ($10^{-3}$ M/ℓ) acts as two-photon absorber.

The two pulses are collimated in a second 50% beam dividing cube. The pump and probe beam are focused into the rhodamine dye samples. The peak intensity of the pump pulse is determined by the energy transmission through a two-photon absorbing rutile crystal [13]. The delayed probe pulse travels at exactly the same path through the dye sample as the pump pulse. Behind the sample, the pulses are separated with a polarizer. The energy transmission of the pump pulse and the perpendicularly polarized probe pulse is measured with photodetectors.

Rhodamine 6G solutions in water, ethanol, ethylene glycol and glycerol and rhodamine B solutions in water, ethanol and glycerol were investigated at room temperature. The rhodamine 6G concentrations were $10^{-5}$ M/ℓ. Dye cells of 2 cm length were used. For the rhodamine B solutions concentrations of $10^{-4}$ M/ℓ and cell length of 0.5 cm were applied.

Energy transmission ratios $T_\perp/T_L$ versus the delay time $t_D$ were measured for all dye solutions. In fig. 2 the results for rhodamine 6G dissolved in water are shown as an example. The peak intensity of the pump beam was $I_{0L} = 1 \times 10^9 \ W/cm^2$. The pulse duration was $t_p \approx 3.7$ ps (fwhm). In fig. 2 the curves are calculated for different relaxation times $\tau$ and for $D_m = 1$, $D_m = 0.93$, and $D_m = 0.85$. For $\tau \gtrsim t_p/3$ a distinct peak in the curves occurs at $t_D \approx t_p/2$. The absorption
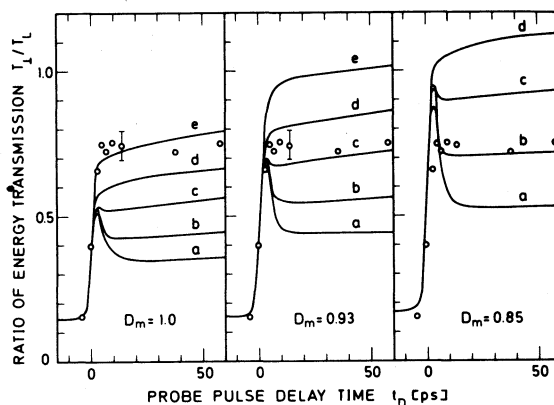


Fig. 2. Normalized energy transmission of perpendicularly polarized probe pulses versus delay time measured for rhodamine 6G dissolved in water. Dye concentration $10^{-5}$ M/ℓ, sample length 2 cm. The circles represent experimental data. The input parameters are pulse duration $t_p = 3.7$ ps, peak intensities $I_{0L} = 10^9 \ W/cm^2$ and $I_{0P} = 6.3 \times 10^7 \ W/cm^2$. The curves are calculated for $D_m = 1$, $D_m = 0.93$, $D_m = 0.85$, for $\tau = 4$ ps (a), $\tau = 2$ ps (b), $\tau = 1$ ps (c), $\tau = 0.5$ ps (d), $\tau = 0$ ps (e), and for $\tau_{or} = 230$ ps [9].

of the probe beam increases when the dye molecules relax from the excited Franck–Condon state. The shape of the curves allows the determination of $\tau$ for $\tau > t_p/3$. In our experiments no peak was found for $T_\perp/T_L (t_D)$. The relaxation time $\tau$ is therefore expected to be shorter than 1.5 ps. The absolute value of the transmission ratio is influenced by the relaxation time $\tau$ and the molecular dichroism $D_m$. The true value of $\tau$ has to be determined by a method that is insensitive of $D_m$. Two such methods were described in ref. [11]. Using the $\tau$ values of ref. [11], the molecular dichroism values $D_m$ are determined from the absolute transmission ratio. For our example in fig. 2 it is $\tau = 0.7 \pm 0.3$ ps and we find $D_m = 0.93 \pm 0.03$.

The energy transmission ratio $T_\perp/T_L$ depends on the peak intensities of the pump and probe beam as shown in fig. 3 for rhodamine 6G dissolved in water (delay time $t_D = 7$ ps). The curves are calculated for $\tau = 0.7$ ps and $D_m = 1, 0.93$, and 0.85. At low intensities the pump beam does not bleach the dye and pump and probe beam suffer the same linear absorption ($T_\perp/T_L \to 1$). In the intensity range around $10^9 \ W/cm^2$ the dye solution is partially bleached by the intense pump beam. The transmission of the probe beam depends on the value of $D_m$. For values of $D_m$
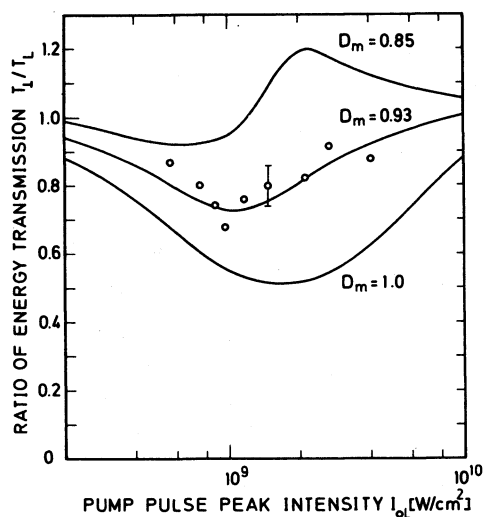
Fig. 3. Intensity dependent energy transmission of perpendicularly polarized probe pulses through a rhodamine 6G solution in water ($10^{-5}$ M/ℓ, $l$ = 2 cm). The circles represent experimental data. The laser parameters are $t_p$ = 3.7 ps and $I_{0L}/I_{0P}$ = 16. The curves are calculated for $\tau$ = 0.7 ps [11] and $\tau_{or}$ = 230 ps [9].

near one ($\sigma_\perp \ll \sigma_\parallel$) the pump pulse preferentially excites molecules oriented under a small angle $\theta$ to the pump pulse polarization. The perpendicularly oriented molecules remain in the ground state and absorb the delayed probe beam. The probe pulse is stronger absorbed than the pump pulse. For small values of $D_m$ the pump pulses also excite molecules oriented perpendicular to the pump polarization. The delayed probe beam suffers less absorption than the pump beam since the molecules are already excited when the probe beam passes through the sample. At very

high intensities the pump pulse promotes all dye molecules to an excited state and pump and probe beams pass through the sample with practically no absorption. The transmission $T_\perp/T_L$ approaches the value of 1 for all values of $D_m$. It is readily seen in fig. 3 that our experimental points are well accounted for by a calculated curve with $D_m$ = 0.93.

In table 1 our experimental results for $D_m$ are summarized together with the parameters $\sigma_M$, $\sigma_{ex,M}$, $\tau_{or}$, and $\tau$. The molecular dichroism is found to be in the range between 0.90 and 0.95.

The theoretical value of $D_m$ = 1 for the linear oscillator model is not found experimentally. This result is in agreement with the fluorescence polarization measurements for very diluted rhodamine 6G and rhodamine B solutions in glycerol [14] ($P_0$ = 0.44) and plexiglas [15] ($P_0$ = 0.46). Deviations from the linear oscillator model are expected for symmetric molecules [5], for overlapping absorption bands with differently oriented transition moments [6], for molecules that execute deformation [6] or torsional vibrations [16], and for transitions that involve magnetic dipole and electric quadrupole transitions [5]. The investigated rhodamine molecules are asymmetric ($C_1$), so the symmetry of the molecules cannot explain the reduced $D_m$ and $P$ values. At the wavelength of the laser pulses ($\tilde{\nu}_L$ = 18 910 cm$^{-1}$) there is only one electronic absorption band expected. The studied transition is allowed for electric dipole transitions; contributions to the absorption from magnetic dipole and electric quadrupole transitions are unlikely. Deformational and torsional vibrations seem to be the most likely process that causes the deviation from the linear oscillator model.

Table 1

| Solution | Conc. (M/ℓ) | $\sigma_M$ (cm$^2$ × $10^{16}$) | $\sigma_{ex,M}$ (cm$^2$ × $10^{17}$) | $\tau_{or}$ (ps) | $\tau$ (ps) | $D_m$ |
|---|---|---|---|---|---|---|
| rhodamine 6G in | | | | | | |
| water | $10^{-5}$ | 3.7 | 5.9 | 230 | 0.7 | 0.93 ± 0.03 |
| ethanol | $10^{-5}$ | 4.2 | 5.9 | 270 | 0.7 | 0.95 ± 0.03 |
| ethylene glycol | $10^{-5}$ | 3.8 | 10 | 2000 | 0.8 | 0.94 ± 0.03 |
| glycerol | $10^{-5}$ | 3.5 | 4.8 | > 2000 | 0.8 | 0.92 ± 0.03 |
| rhodamine B in | | | | | | |
| water | $10^{-4}$ | 1.5 | 5.7 | 230 | 0.9 | 0.90 ± 0.03 |
| ethanol | $10^{-4}$ | 1.6 | 5.3 | 270 | 0.9 | 0.93 ± 0.03 |
| glycerol | $10^{-4}$ | 1.0 | 4.4 | > 2000 | 0.8 | 0.93 ± 0.05 |

The molecules in the ground state populate vibrational states within an energy range of $\Delta E \approx kT \approx 200$ cm$^{-1}$. In the absorption process, transitions from various vibrational levels in the $S_0$ state to vibrational Franck–Condon levels in the $S_1$ state are involved. The orientation of the transition moments for these various vibronic transitions seem to be different. Assuming a spread $\Delta\theta$ of the orientation angles $\theta$ around a mean value $\theta_0$ and using the linear oscillator model one calculates by use of a Taylor expansion

$$\langle \sigma(\theta) \rangle = \sigma \langle \cos^2\theta \rangle = \sigma \langle \cos^2(\theta_0 + \Delta\theta) \rangle$$

$$\approx \sigma [(1 - \langle (\Delta\theta)^2 \rangle) \cos^2\theta_0 + \langle (\Delta\theta)^2 \rangle \sin^2\theta_0] .$$

This formula is identical with the ansatz used in our calculations [$\sigma_\parallel = \sigma(1 - \langle (\Delta\theta)^2 \rangle)$, $\sigma_\perp = \sigma \langle (\Delta\theta)^2 \rangle$]. The measured value of $D_m = 0.93$ is equal to $\sigma_\perp = \sigma(1 - D_m)/2 = 0.035\sigma$ and corresponds to an average angular spread of the transition moments $\Delta\theta = [\langle (\Delta\theta)^2 \rangle]^{-1/2} = 0.19 \approx 10°$. This value is in agreement with results of fluorescence polarization measurements [5,15].

In conclusion we want to emphasize that we have introduced a new technique to determine the absorption anisotropy of dye solutions. In contrast to the common fluorescence polarization technique our method is not limited to highly viscous solvents and low solute concentrations. The measured dichroism was found to be lower than the theoretical value for a linear oscillator model. This behavior is explained by assuming differently oriented transition moments for the transitions from the thermal equilibrium states in the ground state to the respective $S_1$ states.

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