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Light-induced dichroism and birefringence in dye-doped glycerin

I. JÁNOSSY[1] and E. BENKLER[1,2]

[1] *Research Institute for Solid State Physics and Optics - Budapest, Hungary*
[2] *Institute for Applied Physics, Darmstadt University of Technology Darmstadt, Germany*

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Abstract. – In this paper cw laser-induced dichroism and birefringence measurements are reported in azo-dye–doped glycerin at temperatures below −40 °C. The presence of the dye, in combination with the slow rotational mobility of the molecules, leads to a huge enhancement of the optical Kerr effect, compared to what is observed in pure transparent liquids. In the experiments, significant optical anisotropy could be generated at pump intensities as low as 10 mW/mm^2. Evidence is presented that the birefringence signal originates in a large part from the ordering of the host molecules. The orientational order of the solvent molecules is attributed to the guest-host interaction between the azo dye and the glycerin molecules.

Nonlinear optical properties of dye-doped liquids and liquid crystals attracted considerable interest recently. Special attention was paid to light-induced alignment of molecules in isotropic liquids (optical Kerr effect), and optical reorientation in nematic liquid crystals. In the latter system it was discovered more than a decade ago that traces of dichroic dyes considerably enhance the torque exerted by an optical field on the director [1, 2]. Later, using nanosecond laser pulses with high peak intensities, it was shown that an analogous amplification of the optical Kerr effect takes place in the isotropic phase of dye-doped liquid crystals [3–5]. The two phenomena were traced back to the same mechanism. In both cases, the orientationally selective excitation of the dye molecules plays an essential role. Due to this selectivity, the orientational distribution of excited- and ground-state dye molecules exhibits a lower symmetry than the unperturbed system. In (macroscopically) spherically symmetric isotropic liquids, the distribution of the dye molecules becomes axially symmetric in the presence of excitations, the optical axis being parallel to the polarization of the exciting beam. Through guest-host interaction, the asymmetrically distributed dye molecules contribute to the alignment of the host material as well, which is observed as an enhancement of the overall orienting effect of the light beam.

The fact itself that polarized illumination can create an anisotropic distribution of dye molecules in liquids was demonstrated already in 1971 by Makushenko *et al.* [6, 7]. They investigated highly viscous glycerin, doped by azo dyes. In their system trans and cis conformers

of the azo compound played a similar role to ground and excited states of the dye molecules in low-viscosity fluids. At sufficiently low temperatures, the molecular motions slowed down to such an extent that it was possible to induce significant dichroism via trans-cis photoisomerization with a relatively weak cw light source. From the observations, Makushenko *et al.* estimated the angular jump of the transition dipole moment of a dye molecule during a conformational change. More recently, Hartman *et al.* used optically heterodyned polarization spectroscopy to study the rotational diffusion of different solute molecules on a picosecond time scale [8,9]. This method basically also relies on the measurement of the optical anisotropy created by an absorbed light beam.

In the present paper, we reconsider the type of guest-host mixtures studied by Makushenko *et al.* The aim of the work is not only to investigate the alignment of the dye molecules under the influence of irradiation, but to estimate the accompanying ordering effect on the host molecules, too. To gain information on both processes, we measured light-induced dichroism as well as birefringence. At the wavelengths used in the experiments, the host is transparent; therefore dichroism data reflect the properties of the orientational distribution of the dye alone. On the other hand, the measured birefringence is a superposition of contributions resulting from the dye and host molecules. Although in this work we are not able to separate accurately the two contributions, we present evidence that the contribution from the host molecules is at least as important as the one originating directly from the dye. Therefore, we assert that the guest-host interaction between azo dyes and glycerin molecules leads to an ordering of the host molecules simultaneously with the dye orientation, in analogy to the observations in the isotropic phase of liquid crystals.

We investigated glycerin, doped with the azo compounds Disperse Orange 3 (from Aldrich) and Methyl Red (from Merck). The dye concentration was in the range of 10^{-2}% w/w. The cells were 1–2 mm thick and were placed into an optical cryostat, where the temperature could be stabilized to 1 °C. We note that the temperature was not detected directly at the sample and the sample temperature might deviate from the nominal value. In the experiments a pump-probe technique was applied. The pump beam was a linearly polarized 488 nm line from an argon ion laser. The polarization could be set either horizontally or vertically, with the help of a twisted nematic electro-optic cell. The pump intensity was kept constant during the measurements; it was approximately 10 mW/mm^2. The dichroism was measured with a second argon ion laser, also at 488 nm. This beam was polarized at 45° with respect to the pump and was chopped with an acousto-optic modulator, in order to reduce its effect on the light-induced process. Behind the sample, a polarizing beam splitter divided the probe beam into a horizontal and a vertical component. The intensities of the two components were measured with separate detectors, synchronously with the signal from the acousto-optic modulator. A sensitive test of the presence of induced dichroism was obtained by checking if the probe intensities measured by the two detectors were interchanged after switching the pump polarization between horizontal and vertical directions. The birefringence was tested with a He-Ne laser at 633 nm, with the help of a photo-elastic modulator and lock-in detection. This technique allowed us to detect changes less than $\pi/1000$ in the phase shift between the horizontal and vertical components of the He-Ne probe beam. The method provided the sign of the phase shift also, which was expected to change whenever the pump polarization was switched by 90°. None of the beams were focussed; the diameter of the pump beam was 1.8 mm, while the probe beams had smaller diameters and were positioned around the center of the pump.

Reference measurements with a sample filled with pure glycerin did not show any of the anisotropic effects discussed below for the azo-dye–doped samples. In what follows, we present in detail the results of measurements carried out on a 1 mm thick sample, doped with 2×10^{-2}% w/w Disperse Orange 3. At room temperature, upon switching on the pump beam,

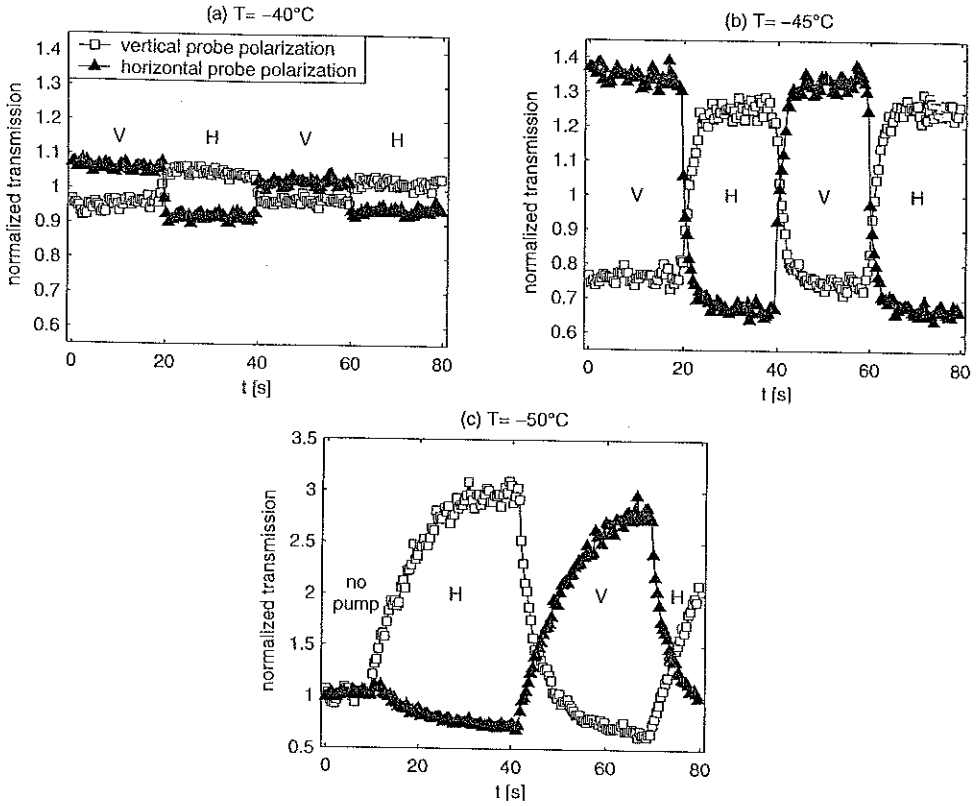

Fig. 1 – Normalized probe transmissions under illumination. H: horizontal pump polarization; V: vertical pump polarization. (a) $T = -40\,^{\circ}\mathrm{C}$, (b) $T = -45\,^{\circ}\mathrm{C}$, (c) $T = -50\,^{\circ}\mathrm{C}$.

the intensity of both components of the argon-ion probe laser increased. The increase can be attributed to the formation of cis isomers, which have smaller absorption cross-sections at this wavelength than the trans ones [10]. The detected changes did, however, not depend on the direction of pump polarization, indicating that no measurable dichroism was induced. Unambiguous evidence of induced dichroism was found at $-40\,^{\circ}\mathrm{C}$. Between $-40\,^{\circ}\mathrm{C}$ and $-50\,^{\circ}\mathrm{C}$, a sharp increase of dichroism was observed (fig. 1). The dichroism was negative, *i.e.* the absorbance was smaller in the direction of the pump polarization than in the perpendicular direction, in accordance with the observations reported in [6,7]. As can be seen from the figure, the response time also increased in the same temperature range, from the limit of the resolution of the measurement ($\approx 0.4\,\mathrm{s}$) to more than 10 seconds. Further cooling of the sample resulted in additional increase of the dichroism and slowing-down of the process.

In the birefringence measurements, a small signal was seen already at room temperature. A part of the signal did not depend on the pump polarization; it may originate from thermally induced flow of the mixture or stress in the glass substrates of the sample. A very small, but systematic modulation of the phase shift ($\approx -3\times10^{-4}\pi$) occurred when the pump polarization was switched. This signal, however, did not change significantly during cooling, down to $-35\,^{\circ}\mathrm{C}$. Between $-40\,^{\circ}\mathrm{C}$ and $-50\,^{\circ}\mathrm{C}$, a large increase of the birefringence took place (fig. 2) similar to what was observed for the dichroism. The birefringence was negative, *i.e.* the optical path was longer for the component of the probe beam polarized perpendicularly to the pump

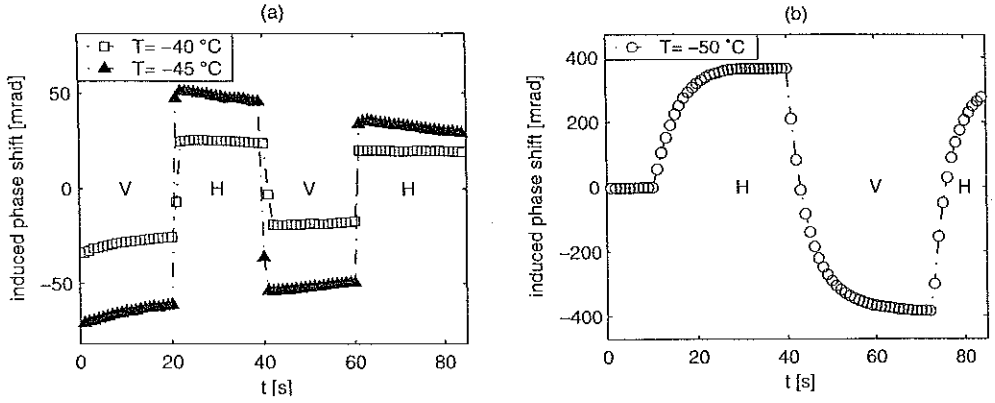

Fig. 2 – Birefringence under illumination. (a) $T = -40\,^{\circ}\mathrm{C}$, $T = -45\,^{\circ}\mathrm{C}$, (b) $T = -50\,^{\circ}\mathrm{C}$. H: horizontal pump polarization; V: vertical pump polarization. Please notice the different scaling of the plots.

beam than for the one polarized parallelly. Again, slowing-down of the development of the anisotropy with decreasing temperature was observed. It is important to note, however, that the relaxation times were different for dichroism and birefringence. As demonstrated in fig. 3, the birefringence signal had a significantly larger response time than the dichroism. Especially striking is the fact that during the reorientation process, following the switch of the pump polarization, the dichroism crossed the zero-line earlier than the birefringence.

A model describing the origin of dichroism was given in [6,7]. In the model both photoinduced *trans-cis* and the *cis-trans* transitions were considered, while thermal transitions were neglected. The orientational redistribution of the dye molecules was attributed to angular jumps of the transition dipole moment, taking place during both kinds of photoinduced transition. It was assumed that the magnitude of the angular jumps is fixed and it is the same for *trans-cis* and *cis-trans* transitions. On the other hand, a jump can occur with uniform probability along any azimuthal angle around the initial direction of the transition dipole moment.

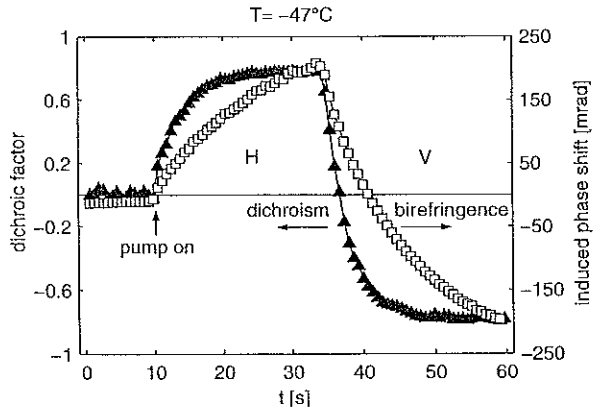

Fig. 3 – Simultaneous measurement of dichroism and birefringence. $T = -47\,^{\circ}\mathrm{C}$. The dichroic factor is defined as $(I_{\mathrm{V}} - I_{\mathrm{H}})/(I_{\mathrm{V}} + I_{\mathrm{H}})$. H: horizontal pump polarization; V: vertical pump polarization.

Under such circumstances, a single jump can equally increase or decrease the angle between the transition dipole moment and the light polarization. In the latter case, however, the dye takes up an orientation in which the molecule is more likely to absorb a photon again than in the first case. Considering a sequence of jumps, one finds that the transition dipole moment of a given dye molecule, on average, rotates in the direction of decreasing absorption probability, *i.e.* away from the light polarization direction. This aligning process is balanced by rotational diffusion, which slows down drastically when the temperature is decreased. Because the aligning mechanism is only weakly temperature dependent, it becomes the dominant process below a certain temperature and leads to the large negative dichroism observed in the experiments.

The Makushenko model is in qualitative accordance with our observations. At room temperature, the thermal relaxation of the metastable cis isomers to the trans state for DO3 is of the order of a second [10]. Cooling down to temperatures below $-20\,^{\circ}\mathrm{C}$ and assuming a scaling with the host viscosity yields a thermal cis life time of several ten minutes or hours, which is indeed the case for other azo dyes [11]. Hence, the thermal cis-trans relaxation can be neglected for the results presented here.

As an alternative explanation one might consider photoinduced crystallization, bulk or surface assisted. It seems, however, unlikely that crystallization could occur in glycerin, which is a very stable supercooled liquid below $+20\,^{\circ}\mathrm{C}$. In addition, crystallization in a supercooled liquid is an irreversible process, therefore the observed anisotropy should have persisted heating up to $+20\,^{\circ}\mathrm{C}$, which was most definitely not the case in our experiments. The different dynamics observed in dichroism and birefringence is also in conflict with a model based on the growth of anisotropic crystals. We note that measurements were performed on several cells, varying the thickness from $200\,\mu\mathrm{m}$ to $2\,\mathrm{mm}$, adjusting the dye concentration in such a way that the absorbance of the cells was approximately the same. All measurements showed similar results, supporting the idea of a bulk mechanism.

In order to interpret the origin of the birefringence, the "direct" contribution of the dye molecules has to be estimated. A rough approximation can be given in the following way. Consider at first a substance consisting purely of trans conformers of the dye, and suppose that these conformers are perfectly aligned. From optical data of crystals and liquid crystals it is known that in such a system the refractive index anisotropy, Δn_0, is not larger than 0.2–0.3. In the dye-doped glycerin we can write

$$\Delta n_{\mathrm{dye}} \approx \Delta n_0 c_d S_d,$$

where Δn_{dye} is the dye contribution to the induced refractive index anisotropy, c_d is the volume fraction occupied by the trans molecules and S_d is their order parameter. We define the order parameter of a certain type of molecules as $S = 1/2\langle 3\cos^2\theta - 1\rangle$, where θ is the angle between the long axis of a molecule and the symmetry axis of the system, here given by the linear polarization of the light that induces the order; $\langle\rangle$ denotes averaging weighted with the orientational distribution of the molecules. We assume that the V-shaped cis isomers do not contribute significantly to the birefringence, because their order parameter is small. To estimate c_d, we suppose that the volume fraction occupied by the dye molecules is equal to their weight fraction (2×10^{-4}). In addition, we estimate the fraction of the trans molecules in the irradiated state to be 50%, which is around the number found for the same dye in the isotropic phase of a liquid crystal under similar irradiation conditions [10]. The negative dichroism suggests that the order parameter is negative, *i.e.* its magnitude can be at maximum 0.5. With these numbers, we find

$$-\Delta n_{\mathrm{dye}} < 1.5 \times 10^{-5}.$$

On the other hand, the measured refractive index anisotropy of the dye-doped glycerin is given as

$$\Delta n = \lambda_{\text{probe}}/2L\frac{\Delta\Phi}{\pi},$$

where $\Delta\Phi$ is the detected phase shift and L is the sample thickness (1 mm). From the birefringence data we see that at $-50\,^{\circ}\text{C}$ and below, $\Delta\Phi/\pi$ exceeds 0.1, hence

$$-\Delta n > 3 \times 10^{-5}.$$

Comparison of Δn_{dye} with Δn suggests that the larger part of the birefringence does not come directly from the dye. It is plausible to assume that this part originates from the alignment of the host molecules.

The above conclusion is strongly supported by observations of the dynamic behavior of the anisotropy (fig. 3). It is evident from the figure that dichroism reaches a steady state faster than birefringence. A straightforward interpretation of this fact is that the alignment of host molecules is delayed with respect to the orientation of the dye. The delay becomes even more evident during the reorientation process, following the switch of the pump polarization. For symmetry reasons, we expect Δn_{dye} to become zero at the moment when the dichroism vanishes. The measured birefringence, Δn, however, has a significant value at this moment, coming fully from the host molecules. A detailed analysis of such kinetic curves may be used to separate quantitatively the dye and host contributions to the birefringence.

As mentioned earlier, in the undoped sample no optical anisotropy was detected. Therefore, the orientational order of the host molecules must originate from their interaction with the dye molecules. On a microscopic scale, the alignment of glycerin molecules by azo dyes should take place independently of irradiation. We suggest that in the unperturbed liquid each dye molecule is surrounded due to hydrogen bonds, which are strengthened on approaching the glass transition at $-88\,^{\circ}\text{C}$, by a number of tightly attached host molecules, forming an anisotropic cluster [12]. In the absence of illumination, the clusters are randomly oriented, therefore no macroscopic anisotropy is observed. The development of macroscopic optical effects in polarized light is due to the orientationally selective destruction of clusters and their reconstruction in a new direction, through the mechanism explained earlier. According to this picture, the delay observed between the dichroism and the birefringence corresponds to the build-up time of the clusters.

The presence of clusters might also explain another fact. According to the Stokes-Einstein-Debye (SED) relation [8, 9], the rotational diffusion coefficient of a solute molecule (D_{rot}) is related to the solvent viscosity (η) as

$$1/D_{\text{rot}} = CV_{\text{eff}}\frac{\eta}{kT}, \tag{1}$$

where V_{eff} is an "effective" volume of the solute molecule and $C \leq 1$ is a dimensionless factor depending on its shape. The viscosity of the solvent can be obtained from the empirical Williams-Landel-Ferry equation

$$\log \eta/\eta_{\text{g}} = -\frac{17.4(T - T_{\text{g}})}{51.6 + (T - T_{\text{g}})}, \tag{2}$$

where, for glycerin, the glass transition temperature, T_{g}, is 185 K and the viscosity at the glass transition, η_{g}, is 9.4×10^{12} poise [13]. Equation (2) yields for the viscosity 0.39×10^5 poise at $-40\,^{\circ}\text{C}$, 1.16×10^5 poise at $-45\,^{\circ}\text{C}$ and 3.92×10^5 poise at $-50\,^{\circ}\text{C}$. The order-of-magnitude increase of the viscosity between $-40\,^{\circ}\text{C}$ and $-50\,^{\circ}\text{C}$ accounts for the sharp increase of the

relaxation time with decreasing temperature, observed in the experiments. On the other hand, for Disperse Orange 3, CV_{eff} can be supposed to be of the order of a few hundred Å^3. With this estimation, one obtains from eq. (1) that $1/D_{\text{rot}}$ should be in the range of milliseconds, in contrast with the detected several seconds. The contradiction between the theoretical estimation and the experimental findings can be apparently resolved if V_{eff} is identified with the volume of a cluster, rather than the volume of a single dye molecule. However, since the intermolecular interactions are complex and there is, *e.g.*, a breakdown of clusters, the dynamics is rather intricate during the reorientation, suggesting that the simple SED model breaks down at least quantitatively.

Finally, we note that in the case of samples doped with Methyl Red, qualitatively similar phenomena were observed as for Disperse Orange 3. Significant light-induced optical anisotropy appeared, however, at somewhat higher temperatures (−30 °C). This fact indicates a stronger guest-host interaction between Methyl Red and glycerin molecules than for Disperse Orange 3, which might be connected with the formation of hydrogen bonds in the case of Methyl Red.

In conclusion, we demonstrated the very strong amplification of the optical Kerr effect in dye-doped glycerin, which makes it possible to induce measurable birefringence using relatively weak cw sources. When the temperature is decreased, the sensitivity further increases, which is accompanied, as usual, with the slowing-down of the material response. By changing the temperature, it is possible to tune the photoinduced effect continuously from quasi-memory behavior (similar to what is observed in glasses [14] and polymers [15]) to very fast response, characteristic to low-viscosity fluids. The results presented in the paper indicate that such measurements can yield important information regarding the nature of the guest-host interaction.

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