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Influence of the type of light polarization on photoinduced processes

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We investigate the influence of the type of light polarization (linear or circular) on the efficiency of non-linear optical processes in photoanisotropic materials. A theoretical model of photoprocesses in materials in which optical non-linearity is related to absorbing centres with intrinsic linear anisotropy is constructed. Theoretical calculations show that the photostationary concentration of the photoproducts (and the mean values of the non-linear changes in optical constants) in these materials is higher if the exciting light is circularly polarized. Experimental results on non-linear processes in samples of fluorescein incorporated in orthoboric acid and in azodye/polymer layers are in good agreement with the theory.

1. Introduction

It is well known that in many of the photophysical and photochemical processes linearly polarized light induces optical anisotropy. This is due to the intrinsic anisotropy of the centres (molecules), participating in the reactions. If the molecules' absorption depends on their orientation with respect to the polarization direction of light, photoprocesses are more efficient for molecules with orientations close to this direction. As a result the photoinduced changes in the macroscopic optical constants of the sample are anisotropic. Photoinduced anistropy is used successfully in polarization holography, because it helps record the interference of two waves with orthogonal polarizations [1, 2]. In addition, the observation and quantitative estimation of photoanisotropy provides information about the structure of the molecules involved in the process, as well as about the photoproducts. In this paper we draw attention to another effect in photoanisotropic non-linear materials – the influence of the type of light polarization, linear or circular (or non-polarized) on the photoequilibrium in non-linear optical processes and hence on the non-linear change in optical constants.

2. Theory

We shall consider a system of anisotropic absorption centres (molecules) of the same type whose axes' directions are uniformly distributed in space. The macroscopic optical constants of such a system are isotropic. The molecules' intrinsic anisotropy is described by the tensor of their polarizability $\alpha_{ij}(\lambda)$, $(i, j = 1, 2, 3; \lambda$ is the wavelength) that for each molecule can be diagonalized in its own coordinate system. We shall consider a simple photoprocess assuming that the molecules can be in two states – a ground state '1' and an excited state '2' with a lifetime τ. Such a photoprocess is described by:

$$\mathrm{d}N_1/\mathrm{d}t = -kIN_1 + \tau^{-1}N_2 \tag{1}$$

where N_1 and N_2 are the concentrations of the molecules in states '1' and '2', respectively, their sum being equal to the total concentration N of the centres ($N = N_1 + N_2$), I is the light intensity and k is the absorption coefficient of the molecules. The absorption coefficient k of an anisotropic molecule can be written in the form:

$$k = C\sum_i |\boldsymbol{D}_i \cdot \boldsymbol{e}|^2 \tag{2}$$

where C is a constant, $\boldsymbol{D}_i$ ($i = 1, 2, 3$) are vectors oriented along the axes of the molecules' own coordinate systems, such that $D_i^2 = \mathrm{Im}(\alpha_{ii})$ and $\boldsymbol{e}$ is the unit polarization vector of light. When the photoequilibrium is reached, $\mathrm{d}N_1/\mathrm{d}t = 0$, and the concentration of the molecule's in the ground state '1' is determined by:

$$N_1 = \frac{N}{1 + kI\tau} \tag{3}$$

As the molecules have different orientations in space the components of $\boldsymbol{D}_i$ in the laboratory coordinate system for each molecule will depend on its orientation. Let us assume that only one of the elements $\alpha_{ii}(\lambda)$, corresponding to the molecule's axis, is different from the others, i.e. $\alpha_{11} \neq \alpha_{22} = \alpha_{33}$. We can write $\alpha_{11} = \alpha_1, \alpha_{22} = \alpha_{33} = \alpha_2$.

If θ and φ are the polar and azimuthal angles, defining the axis direction of a molecule, its vectors $\boldsymbol{D}_i$ are:

$$\begin{aligned} \boldsymbol{D}_1 &= (\cos\theta, \sin\theta\cos\varphi, \ \sin\theta\sin\varphi)\sqrt{\alpha_1} \\ \boldsymbol{D}_2 &= (-\sin\theta, \ \cos\theta\cos\varphi, \cos\theta\sin\varphi)\sqrt{\alpha_2} \\ \boldsymbol{D}_3 &= (0, -\sin\varphi, \ \cos\varphi)\sqrt{\alpha_2} \end{aligned} \tag{4}$$

Let the light propagate along the direction $\theta = 0, \varphi = \pi/2$ (axis OZ). For linear polarization, say along the OX-axis, $\boldsymbol{e} = (1, 0, 0)$, and from (2) and (4) we obtain for k:

$$k^{\mathrm{L}}(\theta, \varphi) = C(\alpha_1\cos^2\theta + \alpha_2\sin^2\theta) \tag{5}$$

For circular polarization $\boldsymbol{e} = \sqrt{2}/2\ (1, i, 0)$ and the coefficient k is:

$$k^{\mathrm{C}}(\theta, \varphi) = \tfrac{1}{2}C[\alpha_1 + \alpha_2 - (\alpha_1 - \alpha_2)\sin^2\theta\sin^2\varphi] \tag{6}$$

From Equation 3, using Equations 5 and 6, we obtain the photoequilibrium distributions $n_1(\theta, \varphi)$ and $n_2(\theta, \varphi)$ of the concentration of molecules in the states '1' and '2' oriented along (θ, φ) for the two considered states of polarization of exciting light. For light linearly polarized along $\theta = \pi/2$ (axis OX) we have

$$\begin{aligned} n_1^{\mathrm{L}}(\theta, \varphi) &= \frac{n_0(\theta, \varphi)}{1 + (p_1\cos^2\theta + p_2\sin^2\theta)} \\ n_2^{\mathrm{L}}(\theta, \varphi) &= n_0(\theta, \varphi) - n_1^{\mathrm{L}}(\theta, \varphi) \end{aligned} \tag{7}$$

and for circularly polarized light

$$n_1^{\mathrm{C}}(\theta,\varphi) = \frac{n_0(\theta,\varphi)}{1+\frac{1}{2}[p_1+p_2-(p_1-p_2)\sin^2\theta\sin^2\varphi]}$$
$$n_2^{\mathrm{C}}(\theta,\varphi) = n_0(\theta,\varphi) - n_1^{\mathrm{C}}(\theta,\varphi) \tag{8}$$

where $n_0(\theta,\varphi)$ is the initial uniform distribution of the molecules, $p_1 = CI\tau\alpha_1, p_2 = CI\tau\alpha_2$. Figure 1a–d illustrates graphically the distributions $n_1^{\mathrm{L}}(\theta,\varphi)$ and $n_1^{\mathrm{C}}(\theta,\varphi)$ before irradiation and after irradiation for two different values of the parameter p. In this figure we have assumed that $p_2 = 0$.

Integration of $n_1(\theta,\varphi)$ over all directions yields the total equilibrium concentration N_1 (and $N_2 = N - N_1$). Figure 2 shows the dependence of the normalized concentrations N_1/N on the parameter p_1 for the case when $\alpha_2 = 0$ (rod-like molecules) curves 1 and 2, as well as N_1/N as a function of p_2 for $p_1 = 0$ (disk-like molecules) – curves 3 and 4. Curves 1 and 3 correspond to exciting light with linear polarization and curves 2 and 4 to exciting light with circular polarization. It is seen that there are significant differences between the equilibrium concentration N_1^{L} reached after irradiation with linearly polarized light, and the concentration N_1^{C} obtained on irradiation with circularly polarized light. In the general case, $\alpha_1 \neq \alpha_2 \neq 0$. When $\alpha_2 < \alpha_1$, we obtain $N_1^{\mathrm{C}} < N_1^{\mathrm{L}}$, the difference being maximum at $\alpha_2 = 0$ (see curves 1 and 2 on Fig. 2). When $\alpha_2 > \alpha_1$ the differences $N_1^{\mathrm{C}} - N_1^{\mathrm{L}}$ are smaller (curves 3 and 4 show N_1^{C} and N_1^{L} for $p_1 = 0$). In all calculations, the initial distribution $n_0(\theta,\varphi)$ of the molecules' axes is assumed to be uniform along all directions. The concentration N_1^{C} (curve 2) obtained on irradiating molecules for which $\alpha_2 = 0$ with circularly polarized light, coincides with N_1^{L} (curve 3), obtained on irradiating molecules with $\alpha_1 = 0$

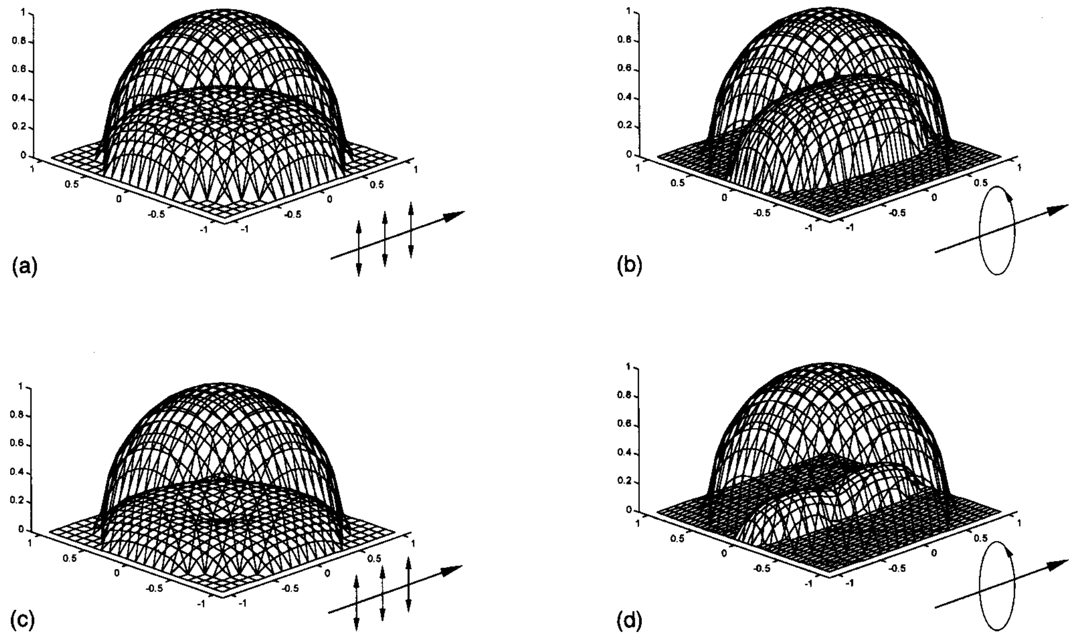

Figure 1 Photoequilibrium distribution $n_1(\theta,\varphi)$ of the molecules oriented along (θ,φ) for the case $p_2 = 0$ before irradiation (spherical distribution) and after irradiation with linearly polarized light: (a) $p_1 = 2$; (c) $p_1 = 10$ and with circularly polarized light: (b) $p_1 = 2$, (d) $p_1 = 10$.

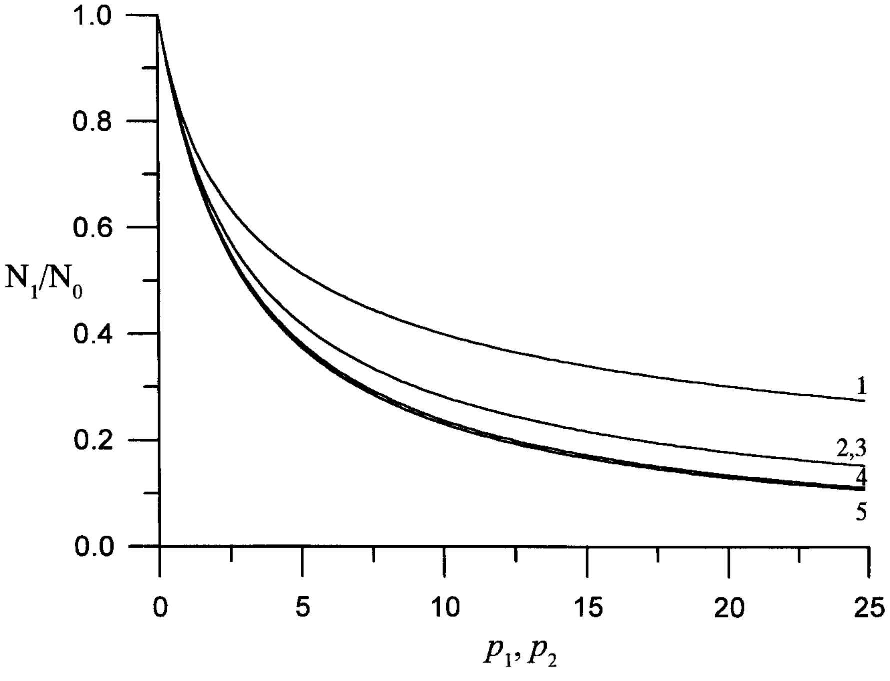

Figure 2 Dependence of the relative photoequilibrium concentration N_1/N on p_1 (for $p_2 = 0$) and on p_2 (for $p_1 = 0$). Curves 1 and 2: $p_2 = 0$, curve 1 is for the case of irradiation with linear polarization, curve 2 for irradiation with circular polarization. Curves 3 and 4: $p_1 = 0$, curve 3 is for the case of irradiation with linear polarization, and curve 4 for that with circular polarization. Curve 5: $p_1 = p_2$.

with linearly polarized light. Curve 5 illustrates the decrease in the photoequilibrium concentration N_1 for the case when $\alpha_1 = \alpha_2$ (isotropic absorption). For isotropic absorbing centres the type of polarization of the exciting light does not influence the photoprocess and $N_1^C = N_1^L$. It should be noted that for isotropic molecules, under otherwise identical conditions (inducing light intensity and lifetime of the excited state '2'), the value of the photoequilibrium concentration N_1 is always lower (and the concentration N_2 is larger).

To calculate the non-linear change in the macrosocopic absorption coefficient of the system we must take into account the photostationary distribution, Equations 7 or 8. If the absorption is assumed to be due only to molecules in the ground state '1', then the absorption in the photoequilibrium state and the optical density D of the sample can be calculated using:

$$D = const. \times \int N_1(\theta, \varphi) \sum_i |e \cdot D_i|^2 \sin\theta \, d\theta \, d\varphi \qquad (9)$$

Here e is the unit polarization vector of the probe beam. If we take the distribution $N_1(\theta, \varphi)$ from Equation 7 – which corresponds to the case when the excitation is made with linearly polarized light, the photoequilibrium optical density of the sample depends on the polarization of the probe beam. It is lowest for linear polarization parallel to the exciting light polarization (D_{par}^L), and highest for the orthogonal linear polarization (D_{ort}^L). For circular polarization of the probe beam or linear polarization at 45° with respect to the

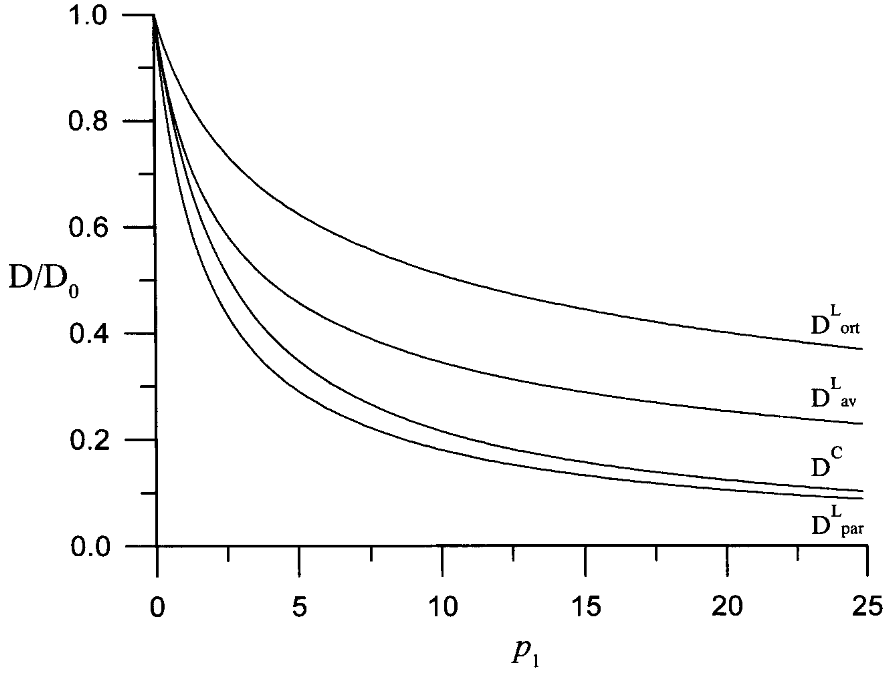

Figure 3 Dependence of the normalized photoequilibrium optical density D/D_0 on irradiation with linearly polarized light: D_{par} is the optical density for polarization parallel to the exciting light linear polarization, D_{ort} is the optical density for the perpendicular polarization, $D_{av} = (D_{par} + D_{ort})/2$ and D^C is the photoequilibrium optical density on irradiation with circularly polarized light.

induced axis, the optical density is $D^L_{av} = (D^L_{par} + D^L_{ort})/2$. Figure 3 shows the dependence of D^L_{par}, D^L_{ort} and D^L_{av} on p_1 (for $\alpha_2 = 0$), as well as the analogous dependence of the photoequilibrium optical density D^C, corresponding to the distribution (8), obtained on irradiation with circularly polarized light. In both cases the probe beam propagates along the direction of the exciting light beam and D^C is independent of its polarization. It is seen that $D^C < D^L_{av}$, that is, the non-linear change in the absorption is larger when induced with circularly polarized light. The difference between the values of D^C and D^L_{av} increases with the increasing of p_1, i.e. at higher values of I and τ. At very high values of p_1, D^C approaches D^L_{par}.

3. Experiments

In order to verify the obtained theoretical results experiments were performed on nonlinear bleaching of two types of materials: a rigid solution of fluorescein in orthoboric acid [3, 4] and azodye methyl red (MR) in a polymer matrix [5].

The absorption maximum of the fluorescein is in the blue region ($\lambda = 455$ nm). On excitation with light in this spectral region its molecules make a transition from ground singlet (S) state into triplet (T) state. A wide T-absorption band in the whole visible region is created. It is known that the fluorescein molecules in the ground state have anisotropic absorption; their absorption is larger for the polarization direction parallel to the molecule axis, that is $\alpha_1 > \alpha_2$. The thickness of the samples was 100 μm. S–T transition was induced in them with an Ar laser beam (λ = 488 nm) with (1) linear and (2) circular polarization and different intensities (0 to 3.2 W cm^{-2}) and measured the non-linear triplet absorption in the red region (outside the S-absorption band). The measurement was performed with a circularly polarized light beam. The results are shown in Fig. 4. It is seen that the non-linear change in optical density is larger at excitation with circularly polarized light as predicted by the theory for the case when $\alpha_1 > \alpha_2$.

The second experiment was performed with 50 μm thick films of MR in a polymethylmetacrylat (PMMA) matrix. Photoprocesses in azodyes are extensively studied mainly because of the high anisotropy that can be induced in them [5–8]. These dyes exist in two isomeric forms – *trans* and *cis*, the former being stable in darkness. The molecules in *trans* form have very strong absorption anisotropy and it is known from the literature [9] that for wavelengths at the maximum of the *trans* absorption band they can be considered as linear dipoles (that is, $\alpha_2 \approx 0$). On illumination with light in the *trans* absorption band a *trans–cis* isomerization by a rotation around the excited double nitrogen bond is initiated. As *cis* molecules absorb in another spectral region, the photoisomerization results in a bleaching of the sample for wavelengths in the *trans* absorption band. The *cis* form is unstable and its lifetime depends on its surroundings, in this case on the matrix in which the dye is introduced. Thus, the photoreaction, taking place with the azodye molecules, resembles the model photoprocess considered by the theory. The absorption maximum of MR is at 450 nm; we illuminated the samples with (1) linearly and (2) circularly polarized light at $\lambda = 488$ nm with different intensities and measured the non-linear changes in the absorption at the same wavelength with a weak probe beam. The propagation direction of the probe beam was at a very small angle with respect to the propagation direction of the

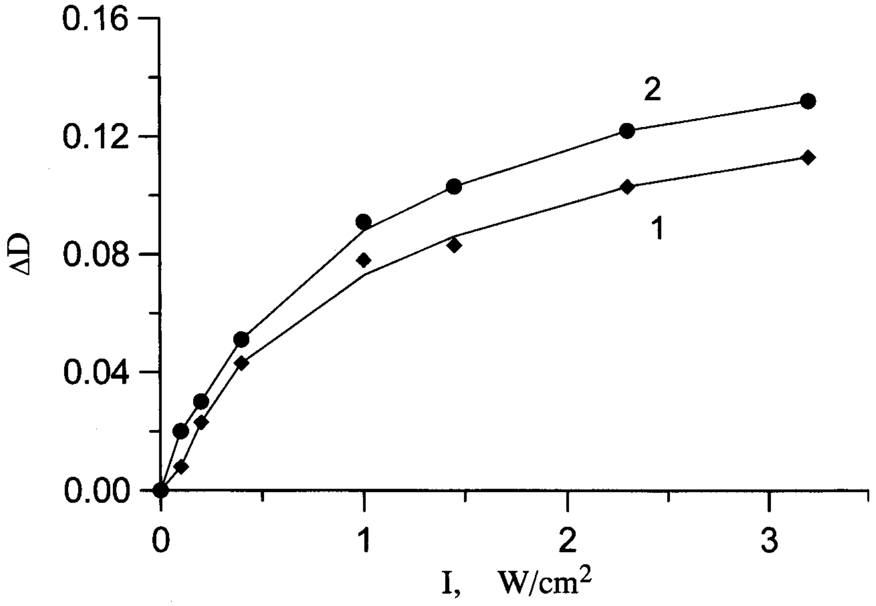

Figure 4 The photoinduced triplet absorption in a sample of fluorescein induced on illumination with an Ar laser beam (λ = 488 nm) with intensity *I* and linear (curve 1) or circular (curve 2) polarization. ΔD is the induced optical density at λ = 633 nm, measured with a circularly polarized He–Ne beam.

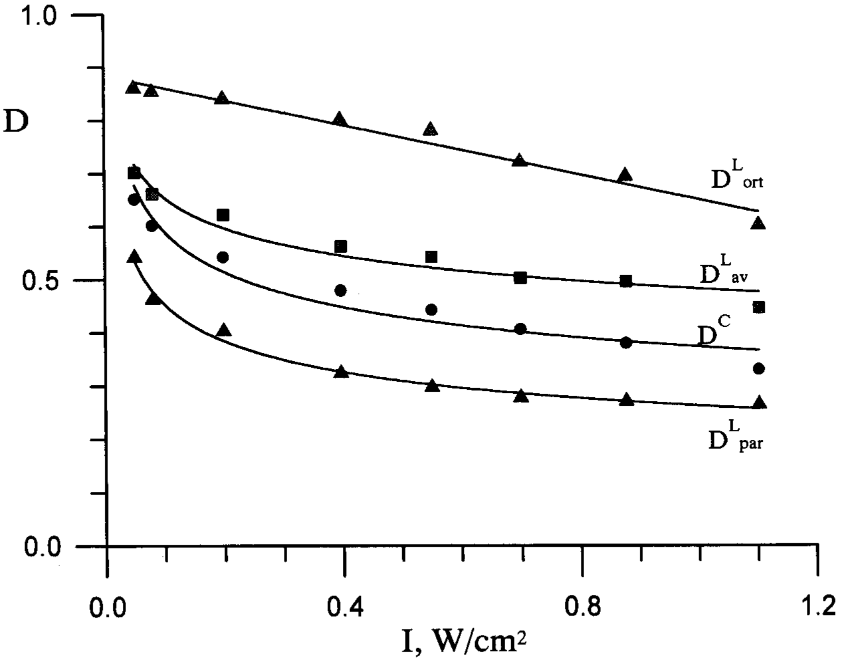

Figure 5 The dependence of the decreasing of the optical density of a sample of MR/PMMA on the intensity *I* of the exciting Ar laser beam. The notations $D^{\mathrm{L}}_{\mathrm{par}}$, $D^{\mathrm{L}}_{\mathrm{ort}}$, $D^{\mathrm{L}}_{\mathrm{av}}$ and D^{C} are the same as in Fig. 3. The probe beam is with λ = 488 nm.

exciting light (~2°). The measurements were made after saturation of the photoinduced changes in the optical density, without turning off the exciting light. The intensity of the probe beam was ~1 mW and it did not induce measurable changes in the absorption. Figure 5 shows the photoequilibrium values of the induced non-linear changes in the optical density of the sample as a function of the exciting light intensity. The curves $D^{\mathrm{L}}_{\mathrm{par}}(I)$, $D^{\mathrm{L}}_{\mathrm{ort}}(I)$ and $D^{\mathrm{L}}_{\mathrm{av}}(I)$ illustrate the changes induced by a linearly polarized light and measured with a beam with the same linear polarization ($D^{\mathrm{L}}_{\mathrm{par}}$), with the orthogonal polarization ($D^{\mathrm{L}}_{\mathrm{ort}}$) and the average value $D^{\mathrm{L}}_{\mathrm{av}} = (D^{\mathrm{L}}_{\mathrm{par}} + D^{\mathrm{L}}_{\mathrm{ort}})/2$. $D^{\mathrm{C}}(I)$ is the intensity dependence of the optical density of the sample corresponding to excitation with circularly polarized light. It does not depend on measuring the light polarization. It is seen again that the average values of the photoinduced non-linear changes are larger on excitation with circularly polarized light. The curves for $D^{\mathrm{L}}_{\mathrm{av}}(I)$ and $D^{\mathrm{C}}(I)$ are very much like the corresponding theoretical curves in Fig. 3.

4. Discussion

The main result from these theoretical and experimental investigations is the establishment and observation of the influence of the type of polarization – linear or circular (or non-polarized) on the values of the non-linear changes in the optical constants of photoanisotropic materials. This influence is larger at high excitation when the concentration of anisotropic absorbing centres in their ground state changes noticeably.

It is worth noticing that the dependence of the optical non-linearity on the type of light polarization – linear (in whatever direction) or circular – must be taken into account when wave mixing in photoanisotropic materials is considered. It results in a secondary effect in the recording of polarization holographic gratings, accomplished with two orthogonal linear light beams – a simultaneous recording of a scalar grating with double spatial frequency. This is due to the kind of light field which results at the interaction of such light beams – for one grating period at equal intensity the light changes its polarization from linear to circular twice. Recording of a grating with double spatial frequency was observed by Solano and Lessard [10] in layers of dyed gelatin plates, and by the authors in similar systems, in azodye/polymer systems and in Ag halide emulsion layers. The effect of doubling the frequency of the recorded polarization gratings appears to be an additional sensitive method of obtaining information about the mechanisms of a large number of photoprocesses, as well as about the structure of the centres taking part in them.

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References

1. SH. D. KAKICHASHVILY, *Polarization Holography* (Nauka, Leningrad, 1989) (in Russian).
2. L. NIKOLOVA and T. TODOROV, *Optica Acta* **31** (1984) 579.
3. T. A. SHANKOFF, *Appl. Opt.* **8** (1969) 2282.
4. T. TODOROV, L. NIKOLOVA, N. TOMOVA and V. DRAGOSTINOVA, *Opt. Quantum Electron.* **13** (1981) 209.
5. T. TODOROV, N. TOMOVA and L. NIKOLOVA, *Opt. Commun.* **47** (1983) 123.
6. T. TODOROV, L. NIKOLOVA, N. TOMOVA and V. DRAGOSTINOVA, *IEEE J. Quantum Electron.* **22** (1986) 1269.
7. Z. SEKKAT and M. DUMONT, *Synthetic Metals* **54** (1993) 373.
8. M. DUMONT, Z. SEKKAT, R. LOUCIF-SÄIBI, K. NAKATANI and J. A. DELAIRE, *Nonlinear Optics* **5** (1993) 395.
9. A. M. MAKUSHENKO, B. S. NEPORENT and O. V. STOLBOVA, *Optika Spectrosk.* **31** (1971) 741.
10. C. SOLANO and R. A. LESSARD, *Appl. Opt.* **24** (1985) 1776.