

Spectral properties of optical anisotropy induced by laser radiation in dye solutions

L G Pikulik, V A Chernyavskii, A F Grib

Abstract. Spectral studies of induced quasi-crystal properties (which can be quantitatively characterised by the difference in the refractive indices of ordinary and extraordinary waves, $\Delta n = n_o - n_e$) in Rhodamine 6G and Rhodamine 4C solutions in glycerine excited in the visible and UV ranges of the absorption spectrum are presented. It is demonstrated that the observed spectral dependences of Δn of these dye solutions excited in the visible (long-wavelength) and UV (short-wavelength) ranges of the absorption spectrum can be interpreted in terms of an oscillator model of a molecule. The proposed method for the analysis of induced optical anisotropy in solutions of organic compounds allows the relative orientation of oscillators in a molecule and, thus, the relative orientation of electronic transitions in a molecule to be determined in a reliable way.

1. Introduction

Papers [1–3] have been devoted to the investigation of spectral dependences of laser-induced optical anisotropy in solutions of organic compounds. These studies have demonstrated that an excited molecular solution displays optical properties similar to the properties of a uniaxial crystal whose axis is determined by the direction of the electric vector in a light wave of pump radiation. The difference $\Delta n = n_o - n_e$ (where n_o and n_e are the refractive indices of ordinary and extraordinary waves, respectively) can be considered to be a quantitative measure of the anisotropy of such a system. Studies have been performed for two organic compounds with different symmetry properties of fluorescence and absorption spectra.

The spectral range of studies was limited by the visible region. Solutions were also excited (for the induction of artificial anisotropy) within the long-wavelength absorption band. The changes in Δn observed under these conditions in both the fluorescence and absorption bands were considered in terms of the well-known theoretical concepts based on oscillator models of molecules and the interaction of oscillators with a radiation driving force. Experimental studies have revealed some universal features in spectral properties of Δn for long-wavelength fluorescent transitions

in a two-level scheme of electronic levels and a four-level scheme of electronic levels.

The purpose of this paper is to investigate the spectral properties of optical anisotropy in dye solutions excited by polarised radiation within the short-wavelength absorption band. The use of polarised excitation in the UV spectral range provides an opportunity to involve new molecular oscillators, which are oriented in the direction orthogonal to the oscillators corresponding to long-wavelength transitions, in the induction of artificial anisotropy. The expansion of the spectral range of studies allowed us to assess the applicability of the oscillator model of molecules in its general form for the description of the anisotropy of excited molecular solutions in both UV and visible spectral ranges.

2. Experimental

Fig. 1 presents an optical scheme of an experiment with a transverse excitation of the solution under study. A more detailed description of this experimental scheme is provided in [4]. We employed the second and third harmonics of radiation of a Nd^{3+} :YAG laser to excite the studied solution and to pump a dye laser, which is used as a source of probe radiation ($E_{\text{pr}}, \lambda_{\text{pr}}$). The duration of Nd^{3+} :YAG-laser pulses was 15–20 ns, and the pulse repetition rate was 1 Hz. The duration of probe pulses was 1–2 ns. We employed probe radiation with a rather low intensity (much less than the intensity of pump radiation) in order to avoid perturbations of the anisotropy state of excited solutions. The content of the quasi-crystal phase in an excited solution was estimated from the Stokes parameters of probe radiation at the output of a cell with the solution [5]:

$$S_0 = I_{\text{pr}}(0, 0) + I_{\text{pr}}(90^\circ, 0),$$

$$S_1 = I_{\text{pr}}(0, 0) - I_{\text{pr}}(90^\circ, 0),$$

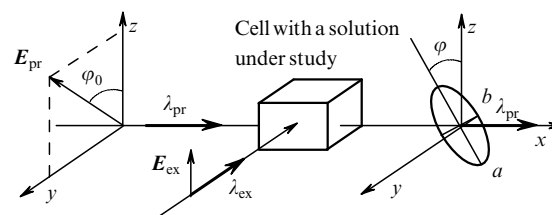


Figure 1. Optical scheme of experiments. The angle ϕ_0 specifies the orientation of the electric vector of probe radiation incident on the solution. The angle ϕ determines the orientation of the principal axis a of the polarisation ellipse at the output of the solution.

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$$S_2 = I_{\text{pr}}(45^\circ, 0) - I_{\text{pr}}(135^\circ, 0),$$

$$S_3 = I_{\text{pr}}(45^\circ, \pi/2) - I_{\text{pr}}(135^\circ, \pi/2),$$

where $I_{\text{pr}}(\theta, \varepsilon)$ are the experimentally measured intensities of probe radiation with different orientation angles of an analyser (the angle θ) and a phase plate $\lambda/4$ (the angle ε). These parameters permit the polarisation state of probe radiation to be estimated and the phase difference δ between ordinary and extraordinary waves to be determined. The modulus of the phase shift between the o- and e-components is given by

$$\tan \delta = \frac{\tan 2\chi}{\sin 2\varphi},$$

where

$$\sin 2\chi = \frac{S_3}{(S_1^2 + S_2^2 + S_3^2)^{1/2}}; \quad \tan 2\varphi = \frac{S_2}{S_1};$$

$$\tan \chi = \pm \frac{b}{a}.$$

The sign of χ determines the rotation direction of an ellipse with semiaxes a and b . For $\chi < 0$, we deal with right-hand rotation ($\delta < 0$ in this case), while for $\chi > 0$, we have left-hand rotation ($\delta > 0$). The difference Δn is determined by the formula

$$\Delta n = \frac{\lambda \delta}{2\pi l},$$

where l is the thickness of the cell in the direction of propagation of probe radiation.

3. Results and discussion

We studied solutions of Rhodamine 6G and Rhodamine 4C in glycerine. This solvent was chosen because the time of Brownian rotational diffusion of dye molecules in a glycerine solution is much greater than the lifetime of these molecules in the excited state. Within the period of time corresponding to the probe pulse, such an excited solution can be considered as a system of rigidly fixed activator molecules.

Consider the experimental results obtained. Open circles in Fig. 2 present the spectral dependence of Δn for a glycerine solution of Rhodamine 6G excited in the UV range of the absorption spectrum at 354 nm. Note that similar results were obtained for a glycerine solution of Rhodamine 4C. The intensity of the fluorescence band and the absorption in the UV and visible spectral ranges are normalised to their maximum values. The ratio of the intensities of the absorption bands in the UV and visible spectral ranges is equal to 1/7.

One can see from Fig. 2 that, with a vertical polarisation of probe radiation, the spectral dependence $\Delta n(\lambda_{\text{pr}})$ can be roughly approximated with a sine function. We also found that $\Delta n < 0$ within the long-wavelength absorption band and $\Delta n > 0$ within the fluorescence band. As we pass from the absorption band to the fluorescence band, negative values of Δn are smoothly and continuously replaced by positive values.

The dependence $\Delta n(\lambda_{\text{pr}})$ observed upon excitation in the UV range of the absorption spectrum at 354 nm is conditionally mirror-symmetric (with respect to the abscissa axis) to the dependence $\Delta n(\lambda_{\text{pr}})$ corresponding to the excitation into the long-wavelength absorption band (closed circles in

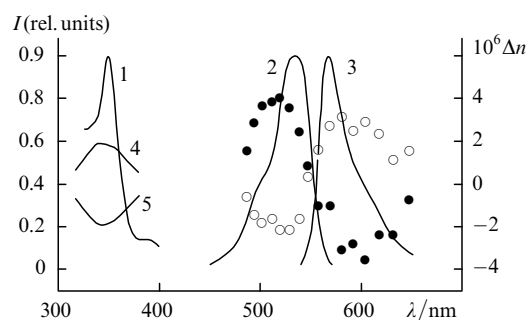


Figure 2. Spectra of absorption (1, 2) and fluorescence (3) bands, spectral dependences of the difference of refractive indices Δn measured for a solution excited within the band 1 (\circ , $\lambda_{\text{ex}} = 354$ nm) and the band 2 (\bullet , $\lambda_{\text{ex}} = 532$ nm), and predictions concerning the spectral dependence of the difference of refractive indices Δn for a solution excited within the UV band (4) and the long-wavelength band in the visible range of the absorption spectrum (5) for the solution of Rhodamine 6G in glycerine with a concentration of dye molecules equal to 5×10^{-5} mol litre $^{-1}$. The intensity of radiation at $\lambda_{\text{ex}} = 354$ and 532 nm is equal to 0.3 MW cm $^{-2}$.

Fig. 2, $\lambda_{\text{ex}} = 532$ nm). The latter dependence was measured in our earlier experiments and was interpreted in terms of the oscillator model of molecules interacting with probe driving radiation [1–3]. Consider the possibility of applying this model to the spectral dependence of Δn measured in the experiments described above, when molecules are excited in the UV range of the absorption spectrum.

First, let us summarise the well-known facts. The oscillators corresponding to the long-wavelength absorption and fluorescence of Rhodamine 6G are parallel to each other, while the oscillator corresponding to the adjacent short-wavelength absorption band is perpendicular to these oscillators [6]. Generally, these oscillators serve as dispersion centres, determining the refractive index of the system. Obviously, the growth in the number of molecular oscillators oriented in the plane corresponding to a given polarisation of a probe light wave increases the refractive index of the solution for this wave. It is well-known that the distribution of excited molecules in the angle η measured relative to the vertical orientation of the electric vector in a light wave of pump radiation is proportional to $\cos^2 \eta$. However, our qualitative analysis of the considered effects will ignore the distribution of molecules in the angle η .

Now, let us examine the dependence $\Delta n(\lambda_{\text{pr}})$ corresponding to the excitation in the UV spectral range. Consider the behaviour of Δn when a solution is excited into the short-wavelength absorption band. When the polarisation vector of pump radiation lies in the vertical plane, molecules with a vertical orientation of the oscillator of short-wavelength absorption are mainly excited in an isotropic solution, while molecules with a horizontally oriented oscillator of short-wavelength absorption and a vertically oriented oscillator of long-wavelength absorption predominantly remain in the ground state. Such a molecular system displays all the properties of optical anisotropy (a quasi-crystal) and, consequently, has different refractive indices for ordinary and extraordinary waves. The interaction of vertically polarised probe radiation with such a molecular system results in the formation of the refractive index n_e , while in the case of a horizontal orientation of the polarisation vector in the probe wave, we deal with the refractive index n_o . Since the relative number of vertically oriented oscillators of long-wavelength absorption is greater than

the number of horizontal oscillators, we arrive at the inequality $n_e > n_o$, and $\Delta n < 0$.

Consider the behaviour of Δn in the fluorescence band. As mentioned above, the oscillator of molecular emission is perpendicular to the oscillator of the short-wavelength absorption. Therefore, due to the internal rearrangement of a molecule initiated by laser excitation, vertically excited oscillators are transformed into horizontally excited oscillators that correspond to the ground fluorescent level. In a system arising as a result of this process, the relative number of horizontally excited oscillators is greater than the number of vertical oscillators, $n_o > n_e$, and $\Delta n > 0$.

The specific features of the behaviour of $\Delta n(\lambda_{pr})$ upon excitation by vertically polarised light wave into the long-wavelength visible absorption band have been considered in detail in Refs [1–3]. The main result of these papers is that excitation into the long-wavelength absorption band depopulates the ground state with vertically oriented molecular oscillators. The relative number of horizontally oriented molecular oscillators becomes greater than the relative number of vertically oriented molecular oscillators, and we deal with a situation when $n_o > n_e$ and $\Delta n > 0$. Molecules with oscillators oriented in the direction parallel to absorption oscillators are transferred to the excited state. The predominant orientation of molecular oscillators under these conditions corresponds to the orientation of polarisation of the pump light wave. Obviously, this polarisation vector lies in the vertical plane. Thus, the number of vertically oriented excited molecular oscillators is greater than the number of molecular oscillators with a horizontal orientation ($n_e > n_o$), and, consequently, $\Delta n < 0$.

Consider now the conditional mirror symmetry of $\Delta n(\lambda_{pr})$ for molecules excited into the long- and short-wavelength absorption bands (see Fig. 2). The results of our studies show that this mirror-symmetric dependence of $\Delta n(\lambda_{pr})$ proves that the oscillators corresponding to the first (long-wavelength) and second (UV) absorption bands are orthogonal to each other. Thus, the method of studying the induced anisotropy in solutions of organic compounds proposed in this paper allows the orientation of molecular oscillators and, thus, the orientation of electronic transitions in a molecule to be determined in a reliable way.

Let us analyse the behaviour of $\Delta n(\lambda_{pr})$ in the second absorption band when molecules are excited into the same band. Because of experimental difficulties, we were not able to measure this dependence. However, taking into consideration the results of the above analysis and the available experimental data, we can readily conclude that Δn should be positive within the entire absorption band. Indeed, the excitation of ground-state molecules decreases the number of molecules with vertically oriented short-wavelength oscillators. Ground-state molecules with short-wavelength oscillators mainly become horizontally oriented. Consequently, we have $n_o > n_e$ and $\Delta n > 0$. Curve 4 in Fig. 2 shows our prediction concerning the dependence $\Delta n(\lambda_{pr})$ in the second absorption band when molecules are excited into the same band. At the same time, excitation into the first long-wavelength band would give rise to a negative spectral dependence of Δn (curve 5).

Let us make certain general remarks regarding the sign of Δn . Crystal optics usually deals with the differences $\Delta n = n_o - n_e$. Therefore, the sign of Δn is determined by the relation between the quantities n_o and n_e . The phase response of solutions (the change in the refractive index) upon high-

intensity isotropic excitation was theoretically analysed in Refs [7, 8]. This analysis predicts that the difference in the refractive indices of nonexcited and excited solutions in the long-wavelength absorption band is positive, while in the fluorescence band, this difference is negative. This prediction qualitatively agrees with the results of experiments [1–3, 9] devoted to the determination of $\Delta n = n_o - n_e$. However, we should emphasise that the above-mentioned experiments were performed with solutions excited with linearly polarised radiation. Naturally, the systems investigated in these experiments were anisotropic. Therefore, the qualitative agreement between the results of theory developed for an isotropic situation and the results of experiments performed on systems with a given anisotropy is, in a certain sense, accidental. If we consider that $\Delta n = n_e - n_o$, the results of the theory mentioned and the experiment would be opposite in sign.

The difference in the orientations of oscillators corresponding to different electronic absorption bands is another important molecular factor. When dye molecules are excited with linearly polarised radiation, orientations of different absorption oscillators in a molecular skeleton can be determined from the change in the sign of Δn . In the case of isotropic excitation, the sign of Δn remains the same for all the absorption bands (Δn is positive within the long-wavelength absorption band in Refs [7, 8]). Indeed, the depopulation of the ground state of dye molecules due to transitions to any higher lying electronic–vibrational level under the action of pump radiation may only decrease the refractive index of the solution as compared to the initial value of the refractive index in a nonexcited solution.

Finally, in the historical context, it would be appropriate to mention papers [10, 11], which were the first to point out an important circumstance that a molecular solution excited with polarised radiation is similar in its optical properties to a uniaxial optical crystal.

To summarise, the results presented in this paper allow us to make a substantially new conclusion that the oscillator model of a molecule, which is successfully employed for the description of the specific features of polarised spontaneous and stimulated emission [6, 12], provides an opportunity to describe and explain the properties of anisotropy (quasi-crystal features) induced by polarised optical radiation in solutions of organic compounds.

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