POLARIZATION OF THE STIMULATED EMISSION OF PHTHALIMIDE SOLUTIONS

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POLARIZATION OF THE STIMULATED EMISSION OF PHTHALIMIDE SOLUTIONS

The study of the anisotropy of the stimulated emission of dye solutions began comparatively recently. To date, measurements have been carried out for only a few compounds. Thus, 100-percent polarization of the stimulated emission of alcoholic solutions of AlCl-phthalocyanine and 3,3′-diethylthiatricarbocyanine iodide was reported under transverse pumping by ruby optical quantum generator light polarized perpendicular to the axis of the liquid-laser resonator (^{1}). Somewhat later, the polarization of the generation of an alcoholic solution of rhodamine 6G was measured at two excitation wavelengths (^{2}). Upon excitation in the long-wavelength absorption band ($\lambda_v = 530$ mμ), the degree of polarization was 100%; pumping in the second absorption band ($\lambda_v = 347$ mμ) gave a polarization of −90%. In (^{3}), completely polarized radiation was obtained from alcoholic and glycerol solutions of cryptocyanine and AlCl-phthalocyanine, and a theoretical explanation of the results obtained was given. In the interpretation, a scheme of two electronic levels with continuous bands of vibrational sublevels was used, ordinarily applied for determining the parameters of liquid optical quantum generators (^{4}). In the calculation (^{3}) it was assumed that the emitter molecules are distributed isotropically and are rigidly fixed, i.e., from the moment of excitation until the generation process they retain their position. As the authors indicated, the conclusions of the work are strictly valid only for viscous solutions. However, they were also in agreement with the results obtained for low-viscosity alcoholic solutions.

It should be noted that the molecules investigated in (^{1}-^{3}) have rather large volumes. Therefore, both in viscous and in nonviscous solutions, during the time that elapses from the moment of excitation to generation, the molecules do not have time to rotate appreciably and disturb the anisotropy created by the exciting light. For such cases, calculations based on the model of rigidly fixed dipoles are valid, and the effect of viscosity on the polarization of generation does not appear.

In the present work, the polarization of stimulated emission is investigated in an important class of luminescent compounds—phthalimides. Generation in solutions of the indicated compounds was obtained by us comparatively recently ([5], [6]). The work studies the effect of viscosity on the polarization of generation radiation. The viscosity was varied by changing the solvent at room temperature, and also by changing the temperature of viscous solutions. As the objects of investigation, 3-amino-N-methylphthalimide, 4-amino-N-methylphthalimide, and 3,6-diamino-N-methylphthalimide were used. The concentration of the solutions studied was chosen to be as low as possible and was approximately 10^{16}—10^{17} cm^{-3}.

The cuvette with the substance under investigation was placed in a resonator with dielectric mirrors. The reflection coefficients of the mirrors were approximately 98% in the region 410–580 mµ. Excitation was carried out with completely polarized radiation of the second harmonic of a single pulse of a ruby optical quantum generator.

A transverse pumping configuration was used. The electric vector of the exciting light was perpendicular to the axis of the resonator. The polarization was measured by a photographic method. A calcite crystal was used as the analyzer. The contrast coefficient of the photographic material was determined under pulsed illumination, i.e., under the same conditions in which the polarization was recorded. In all polarization measurements the level of the exciting light did not exceed the generation threshold by more than a factor of 2. (According to the data of work (2), exceeding the threshold by more than a factor of 4 can cause depolarization of the stimulated emission.) The exciting light was attenuated by light filters. Control measurements of the degree of polarization of an alcoholic solution of Rhodamine 6G gave a result in good agreement with the data of work (2) ($\lambda_\text{v} = 347$ mμ, $P = -90\%$).

Table 1

Dependence of the degree of polarization of the stimulated emission of 3-amino-*N*-methylphthalimide (P_1) and 4-amino-*N*-methylphthalimide (P_2) on the viscosity of the solvents

Solvent	η, cP	P_1, %	P_2, %
Acetone	0.3	–	20
Water	1.02	12	–
Dioxane	1.2	–	21
Ethanol	1.2	12	26
Acetic acid	1.21	14	–
Isobutanol	3.94	20	45
Octyl alcohol	8.8	27	60
Ethylene glycol	17.24	35	–
Cyclohexanol	28	50	88
Glycerin	689	95	96

The viscosity of the solutions was measured with an Ostwald capillary viscometer.

The studies carried out in the present work showed that the degree of polarization of the stimulated emission of phthalimides varies over a wide range when the solvent is changed (see Table 1). Emission with a polarization close to 100% was obtained at room temperature only in the case of glycerin solutions of 3-amino-*N*-methylphthalimide and 4-amino-*N*-methylphthalimide. It should be noted that for these compounds the excitation wavelength of 347 mμ lies in the region of the long-wavelength absorption band, i.e., in this case the absorption and emission oscillators coincide. Therefore, the smaller polarization values in other solvents, in which similar conditions for excitation and emission hold, are not associated with noncoincidence of the absorption and fluorescence oscillators. For 3,6-diamino-*N*-methylphthalimide in glycerin, excitation of generation falls in the region of overlap of the long-wavelength and short-wavelength absorption bands. As a result, simultaneous excitation of two electronic levels occurs, the transitions to which are modeled by two mutually perpendicular oscillators, and the polarization even in a viscous solvent at room temperature is only 45%.

Table 1 compares the polarization of the stimulated emission of 3-amino-*N*-methylphthalimide and 4-amino-*N*-methylphthalimide with the viscosity of the solvents used. Analysis of the data shows that, for both compounds, an increase in viscosity leads to an increase in the degree of polarization; moreover, the magnitude of the polarization of the stimulated emission is probably determined mainly by the value of the viscosity and does not depend on the nature of the solvent. Thus, for 3-amino-*N*-methylphthalimide in water, ethanol, and acetic acid, whose viscosities differ only slightly, approximately identical polarization values were obtained. The same phenomenon is also observed for 4-amino-*N*-methylphthalimide in acetone, dioxane, and ethanol.

As can be seen from Table 1, in the case of 4-amino-*N*-methylphthalimide the change in polarization with viscosity occurs somewhat more slowly than for 3-amino-*N*-methylphthalimide. For example, in isobutanol the degree of polarization of the generation of 4-amino-*N*-methylphthalimide is more than twice as large as the same value for 3-amino-*N*-methylphthalimide. It may be assumed that this difference in the polarization of the stimulated emission of the two isomers is due to a difference in their effective volumes in solutions. Obviously, an increase-

an increase in the volume of the molecule leads to a decrease in its mobility in solution and, consequently, to a relatively greater preservation of the anisotropy of the excited centers up to the moment of generation.

This assumption agrees with the results obtained in the study of the polarization of the fluorescence of phthalimides (^{7}). According to these data, the volume of the molecule of 4-amino-N-methylphthalimide with its solvation shell in isobutyl alcohol (V = 920 cm^3) is more than 3.5 times greater than the volume for 3-amino-N-methylphthalimide (V = 261 cm^3).

Fig. 1. Dependence of the degree of polarization of stimulated radiation P_{gen}

Fig. 1

Figure 1: Fig. 1

and fluorescence P_{fl} of 3-amino-N-methylphthalimide in glycerol on temperature

Fig. 2. Dependence of the degree of polarization of stimulated radiation on the viscosity of 4-amino-N-methylphthalimide (1) and 3-amino-N-methylphthalimide (2). a—solutions at room temperature (see Table 1); —solutions in cyclohexanol (curve 1: $t = 30, 50, 60^\circ$; curve 2: $t = 30, 40, 50, 80^\circ$); —solutions in glycerol ($t = 40, 50, 60, 70, 80, 100, 120^\circ$)

The change in the viscosity of a solution can be produced by changing its temperature. In the present work, the dependence of the degree of polarization of the stimulated radiation of 3-amino-N-methylphthalimide in glycerol and cyclohexanol, of 3,6-diamino-N-methylphthalimide in glycerol, and of 4-amino-N-methylphthalimide in cyclohexanol on the temperature of the solution was investigated. In Fig. 1, as an example, the course of the temperature change in the generation polarization of 3-amino-N-methylphthalimide is shown. The temperature change in the fluorescence polarization is also presented there. It is evident from the figure that the temperature change in the polarization of the stimulated and spontaneous radiation has a similar character. First of all, in both cases the curves $P(t)$ have saturation regions. The limiting polarizations that are reached at saturation in both cases are close to P_{lim} ($P_{\text{lim}}^{\text{gen}} = 100\%$, $P_{\text{lim}}^{\text{fl}} = 50\%$), which indicates coincidence of the absorption and emission oscillators in the molecule. Increasing the temperature causes a decrease in the polarization of both the stimulated and spontaneous radiation. However, as can be seen from the figure, the indicated dependences also have certain differences. Saturation of the polarization occurs at different temperatures. The fluorescence polarization begins to decrease at $t = -20^\circ$, whereas the generation polarization begins to fall only at $t = +45^\circ$. This is evidently due to the shorter duration of the excited state in the case of stimulated radiation. Further, an increase in temperature leads to complete depolarization of the fluorescence. The stimulated radiation at $t = +120^\circ$ is still partially polarized.

In the case of solvents of lower viscosity, such as cyclohexanol, the change in polarization occurs approximately in the same way as in glycerol. The only difference is that, because of the relatively small value of the viscosity at room temperature, the decrease in polarization begins—

appears immediately upon heating the solution. The polarization values of the stimulated emission of 3-amino-N-methylphthalimide and 4-amino-N-methylphthalimide corresponding to different temperatures are shown in Fig. 2.

The change in the polarization of the stimulated emission of phthalimide derivatives when the solvent is changed at room temperature and when the temperature of viscous solutions is changed is explained by us as being due to a greater or lesser degree of rotation of the molecules before the moment of generation. If this hypothesis is correct, one may expect that the degree of polarization of the generation emission will be determined mainly by the viscosity of the solvent used. (It should be borne in mind that in the cases studied the relative change in temperature is small in comparison with the change in viscosity.) Figure 2 shows the dependence of the degree of polarization of the stimulated emission of 3-amino-N-methylphthalimide and 4-amino-N-methylphthalimide on the viscosity of the solvent. The viscosity interval from 1 to 28 cP is covered by changing the solvent at room temperature, and from 3 to 140 cP by changing the temperature of glycerol and cyclohexanol solutions. As can be seen from the figure, the experimental points are combined by a common curve, i.e., the magnitude of the polarization of the stimulated emission in the cases studied is determined primarily by the viscosity of the solution.

Thus, the study carried out in the present work shows that the polarization of stimulated, as well as spontaneous, emission may depend on the viscosity of the solvent. The dependence of the polarization of generation emission on the viscosity of the medium indicates that the assumption of rigidly fixed emitting molecules when considering the polarization of stimulated emission [3] is not always justified. For compounds whose molecular volumes are 4–5 times smaller than the volumes of the dye molecules studied in works [1–3], despite the fact that during stimulated emission the molecule in the excited state exists for a time shorter than τ_{fl}, rotational depolarization of the generation emission takes place.

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