

Exceeding the classical limit of the degree of polarization under the nonlinear Hanle effect of diatomic molecules

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The limiting values of the degree of linear polarization of fluorescence in diatomic molecules, brought about by the Hanle effect of the ground state under conditions of optical detuning, is studied. Using classical representations as well as polarization moments, the physical reasons for exceeding the degree of polarization, above the maximum under weak light excitations of *P*- and *R*-type transitions with $P = 1/7$, have been discovered.

1. INTRODUCTION

In the first works of Hanle¹ it was already known that a decrease in the degree of linear polarization of resonance fluorescence in atoms occurs on superposition of an external magnetic field **H**, perpendicular to the **E** vector of the exciting radiation (the Hanle effect), caused by the precession of damping oscillators about **H**. This results in a depolarizing action of the magnetic field, transverse to **E**, as opposed to the repolarizing action of the longitudinal field **H**||**E** in the presence of hyperfine structure (for example Ref. 2). The above is true for a response linear, with respect to the light field, of an ensemble of particles under weak light excitation, when one can assume that the distribution of angular momenta of the ground state remains isotropic. If this is not the case, we are considering optical pumping, in particular optical detuning of the ground state,³ where one can observe the Hanle effect of the ground state.⁴ An interesting case, assuming a graphic classical interpretation, is laser optical detuning by destruction of diatomic molecules with large angular momenta, according to Fig. 1 (Refs. 5–7). This effect leads to a decrease in the degree of polarization of fluorescence $b \rightarrow c$. The transverse magnetic field, under specific conditions, is capable of again raising the degree of polarization due to partial destruction of detuning on precession of the moments of the lower state about **H**, making it possible to observe, in the fluorescence, the Hanle effect of the ground state in diatomic molecules. Such an effect was discovered and studied in Refs. 8–11. In this case¹⁰ it was discovered that for *P*- and *R*-type transitions ($J' = J'' \pm 1$), the field **H**||**E** not only restores the degree of polarization of fluorescence in Te_2 vapor to the maximum possible value, $P = 1/7$, in linear response as $J \rightarrow \infty$, but also leads to values larger than $1/7$. The recorded effect of repolarizing of the transverse field during optical detuning, which partially compen-

sates the depolarizing influence of the molecule's intrinsic rotation, is considered in the present paper in a graphic classical model of rotating oscillators and with the aid of polarized moments.

CLASSICAL TREATMENT

Let a linearly polarized (**E**||**X**) laser beam, directed along **Y** [Fig. 2(a)], excite a resonance transition $a \rightarrow b$ at a rate Γ_p in a molecule (Fig. 1). On optical pumping by destruction one can assume that due to the large number of resolved transitions to the initial vibrational–rotational level v''_a, J''_a from v'_b, J'_b , by radiative methods, an insignificantly small portion of the molecules rotate, and their detuning is determined by the fact that the rate of absorption Γ_p compensates with the rate of nonradiative relaxation γ between the crowded v'', J'' sublevels, i.e., $\Gamma_p \sim \gamma$. Here we will neglect the induced transitions $b \rightarrow a$, assuming that the overall rate of decay Γ of the *b* state is much greater than Γ_p .

We will proceed from the classical representation of oscillating dipoles **p**, which in the case of *P*- or *R*-type transi-

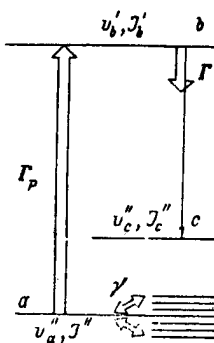


FIG. 1. Diagram of optical pumping.

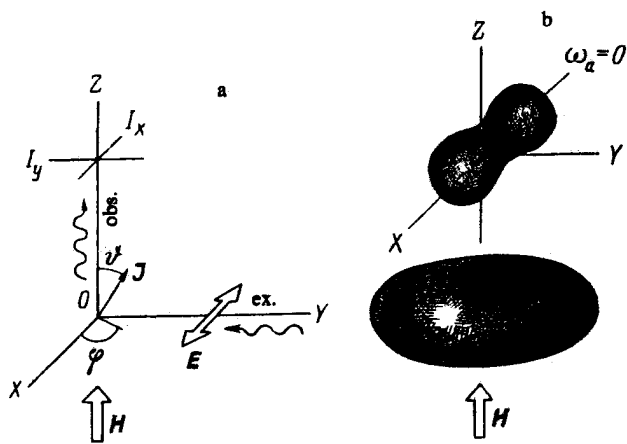


FIG. 2. a—diagram of excitation and observation of fluorescence, b—distribution of angular momenta $J_a(\vartheta, \varphi)$ in the absence of a magnetic field $\omega_a = 0$ and for a large field $\omega_a/\gamma > 1$.

tions are located in the rotational plane of the internuclear axis and rotate together with the molecule, remaining perpendicular to the angular momentum vector \mathbf{J} . We will write down the balance equation, following Refs. 7, 9, and 10, for the concentration density $n_a(\vartheta, \varphi)$ of the molecules in the state a with angular momentum $J_a(\vartheta, \varphi)$ [Fig. 2(a)], assuming that the molecule's period of intrinsic rotation is much less than the characteristic time for all relaxation processes

$$n_a(\vartheta, \varphi) = -\Gamma_p n_a(\vartheta, \varphi) C_X^{\text{abs}}(\vartheta, \varphi) + \lambda_a - \gamma n_a(\vartheta, \varphi) - \omega_a \frac{\partial n(\vartheta, \varphi)}{\partial \varphi}. \quad (1)$$

Here the first term of the right-hand side describes the absorption, $C_X^{\text{abs}} = (1 - \sin^2 \vartheta \cos \varphi)/2$ is the coefficient of the angular probability dependence of P and R absorption for the geometry in Fig. 2(a).² The terms λ_a and γn_a are the number of events in units of population and destruction time for the a level. The last term describes the precession of angular momenta in the magnetic field with frequency $\omega_a = g_a \mu_0 H / \hbar$, where g_a is the Lande g factor, μ_0 is the Bohr magneton. It is assumed that the precession in the excited b state can be neglected, i.e., $\omega_b \ll \Gamma$. The intensity I_i of the fluorescence $b \rightarrow c$ (Fig. 1), linearly polarized along the axis $i = X$ or Y , is expressed by

$$I_i = \int_0^{2\pi} \int_0^\pi n_a(\vartheta, \varphi) C_X^{\text{abs}}(\vartheta, \varphi) C_i^{(1)}(\vartheta, \varphi) \sin \vartheta d\vartheta d\varphi, \quad (2)$$

where $C_X^{(1)}(\vartheta, \varphi) = C_X^{\text{abs}}(\vartheta, \varphi)$, $C_Y^{(1)}(\vartheta, \varphi) = (1 - \sin^2 \vartheta \times \sin^2 \varphi)/2$ (see Ref. 2).

Let the magnetic field be absent, $H = 0$. For $\dot{n}(\vartheta, \varphi) = 0$, from Eq. (1) we obtain

$$n_a(\vartheta, \varphi) = \frac{\lambda_a/\gamma}{1 + C_X^{\text{abs}}(\vartheta, \varphi) \Gamma_p/\gamma}. \quad (3)$$

The form of the distribution for $\Gamma_p/\gamma \sim 3$ is illustrated in Fig. 2(b). It is obvious that the momenta $J_a(\vartheta, \varphi)$ preferentially detune along the \mathbf{E} vector of the exciting radiation. We will now consider how the degree of polarization varies for such a distribution in comparison to an isotropic distribution

$$P = \frac{I_X - I_Y}{I_X + I_Y} \quad (4)$$

for fluorescence observed along the Z axis. Among the absorbing oscillators that rotate about $J_a(\vartheta, \varphi)$, p is smaller than those that rotate in the XY and XZ planes. Oscillators rotating in the YZ plane, perpendicular to \mathbf{E} , dominate and, therefore, do not experience absorption. Recall that the probability of absorption is proportional to $(\mathbf{E} \cdot \mathbf{p})^2$. It is easy to see that having undergone absorption, they will provide a large contribution to I_Y [Fig. 2(a)], and will not contribute to I_X , since they are perpendicular to the X axis. From Eq. (4) it is clear that this leads to a decrease in the degree of polarization P as compared to $P = 1/7$ for an isotropic distribution; this was observed experimentally in Ref. 10. An analytical expression for P as a function of Γ_p/γ , in the absence of a magnetic field, i.e., $\omega = 0$, can be obtained from Eqs. (2)–(4) in the form

$$P^{(P, R)}(\omega = 0) = \frac{(3b^2 - 4b + b^{-1}) \operatorname{arctanh}(b^{-1}) - 3b}{(b^3 - 4b + 3b^{-1}) \operatorname{arctanh}(b^{-1}) - b^2 + \frac{11}{3}}, \quad (5)$$

where $b^2 = 1 + \gamma/\Gamma_p$.

Let us now consider a magnetic field $\mathbf{H} \parallel \mathbf{Z}$ of such strength that $\omega_a/\gamma > 1$, and $\omega_b/\gamma < 1$. This means that the anisotropy of the distribution $J_a(\vartheta, \varphi)$ in the XY plane disappears [Fig. 2(b)], but at the same time the precession of the angular momenta $J_b(\vartheta, \varphi)$ of the excited state, as before, can be neglected. This is possible when $g_a/\gamma > g_b/\Gamma$, which is satisfied, for example, in the vapor of the diatomic molecules Te_2 , Se_2 , K_2 , Na_2 etc.,^{9,10} where the Hanle contour of the ground state is much narrower than that of the excited state.

In Fig. 2(b) it is obvious that in this case the angular momenta $J_a \parallel \mathbf{Z}$ remain discriminant, i.e., the number of absorbing oscillators rotating in the XY plane decreases. And such oscillators, being excited primarily along $\mathbf{E} \parallel \mathbf{X}$ due to rapid rotation, are equally likely to emit the I_X component, polarized along \mathbf{E} , as well as the orthogonally polarized component I_Y , thereby transferring excitation from I_X to I_Y . By the way, this rotation is determined by the value of $P^{(P, R)}(\omega = 0) = 1/7$, in the classical limit of linear response for P and R transitions, as opposed to $P^{(Q)}(\omega = 0) = 1/2$, in the model of stationary oscillators for Q transitions ($J'' = J'$). Consequently, as is the case in Fig. 2(b) for $\omega_a/\gamma > 1$, the decrease in the number of oscillators $p \perp \mathbf{Z}$ must lead to values of the degree of polarization $P^{(P, R)}(\omega_a/\gamma > 1, \omega_b/\Gamma < 1) > 1/7$. This qualitative picture is confirmed by the analytical expression

$$P^{(P, R)}(\omega_a/\gamma \gg 1, \omega_b/\Gamma \ll 1) = \frac{(a^3 + 2a + a^{-1}) \operatorname{arctan} a^{-1} - a^2 - \frac{5}{3}}{(2a^3 - 4a + 2a^{-1}) \operatorname{arctan} a^{-1} - 2a^2 + \frac{14}{3}}, \quad (6)$$

where $a^2 = 1 + 4\tau/\Gamma_p$. Equation (6) is obtained from Eqs. (2)–(4) by averaging over the angle φ in Eq. (3), due to the rapid precession of $J_a(\vartheta, \varphi)$ about \mathbf{H} . The maximum value for the degree is obtained from Eq. (6) as $\Gamma_p/\gamma \rightarrow \infty$ and is equal to $P^{(P, R)}(\omega_a/\gamma > 1, \omega_b/\Gamma < 1) = 1.5 \operatorname{arctan} 1 - 1 = 0.1781$.

We will now trace how the effect of transverse repolarization is associated with the creation of pumping of the polarized moments (PM) of the ground state φ_q^x by light and their connection with PM of the excited state f_Q^K (K and x are the ranks of the tensors, Q and q are their projections^{4,13}). The kinetic equations for φ_q^x and f_Q^K ^{12,14} is written in the limit¹⁵ as $J \rightarrow \infty$ in a symmetric form, which is convenient for computer calculation

$$f_Q^K = \Gamma_p \left(\sum_{q'} D_q^K \varphi_{q'}^x - \sum_{q'} D_{q'}^K f_Q^K \right) - (\Gamma_K - i\omega_b) f_Q^K, \quad (7a)$$

$$\dot{\varphi}_q^x = \Gamma_p \left(\sum_{KQ} D_Q^K f_Q^K - \sum_{q'} D_{q'}^x \varphi_{q'}^x \right) - (\Gamma_x - iq\omega_a) \varphi_q^x + i\lambda_{q'}^x \delta_{q,q'} \varphi_{q'}^x, \quad (7b)$$

where we introduce the notation

$$D_{q'}^x = (-1)^{\Delta} \sqrt{\frac{2x'+1}{2x+1}} \sum_X \sqrt{2X+1} C_{1\Delta 1-\Delta}^{X0} C_{X0 x0}^{X'0} C_{X-q' x' q}^{Xq} \Phi_{q-q'}^{\Delta}(\mathbf{e}). \quad (8)$$

Here $C_{cd\epsilon f}^{ab}$ are Clebsch-Gordan coefficients, $\Delta = J'_b - J''_a$, and the tensor $\Phi_{\Delta}^x(\mathbf{e})$ was presented in Refs. 4 and 13 for various directions of the unit polarization vector \mathbf{e} of the pumping light. In Eq. (7) the induced transitions $b \rightarrow a$ are taken into account.

Remember that the PM of the $K, x = 0$ rank characterize the population density (in the given normalization they coincide with the concentration), and in the $K, x = 2$ rank they characterize detuning. In the geometry of Fig. 2(a), only PM of the even rank can be created. Under conditions of nonlinear optical pumping (here detuning), PM of the ground state with $x = 0$ are created.

The intensity of the radiation at the $b \rightarrow c$ transition with polarization, characterized by the vector \mathbf{e}' , in the limit as $J \rightarrow \infty$, is expressed as¹⁵

$$I(\mathbf{e}') \sim (-1)^{\Delta'} \sum_K \sqrt{2K+1} C_{1-\Delta' 1\Delta'}^{K0} \sum_Q (-1)^Q f_Q^K \Phi_{-Q}^{\Delta'}(\mathbf{e}'), \quad (9)$$

where $\Delta' = J'_b - J''_c$.

The expression for the degree of polarization in the geometry described in Fig. 2(a), for P and R transitions, has the form

$$P^{(P, R)} = \frac{\sqrt{6} \operatorname{Re} f_2^3 / f_0^3}{2 + f_2^3 / f_0^3}. \quad (10)$$

If the same conditions exist as in the classical Eq. (6), i.e., $\omega_a / \tau \gg 1$ and $\omega_b / \Gamma \ll 1$, then the external field H destroys all the transverse components of detuning of the lower state φ_q^x with $q \neq 0$, but does not influence the moments $f_{\pm 2}^2$, and Eq. (10) in this limit can be written via the moments φ_0^x

$$P^{(P, R)} (\omega_a / \tau \gg 1, \omega_b / \Gamma \ll 1) = \frac{7 - 10\varphi_2^3 / \varphi_0^3 + 3\varphi_4^3 / \varphi_0^3}{49 + 50\varphi_2^3 / \varphi_0^3 + 6\varphi_4^3 / \varphi_0^3}. \quad (11)$$

Note that under weak excitation, when $\Gamma_p / \gamma \ll 1$, only PM of zero rank are present in the lower state and the degree of polarization is equal to the classical value 1/7. If this is not the case, i.e., optical pumping of the a level occurs, then the resulting moments φ_q^x may be calculated using a computer, to solve the system (7).¹⁵ The results of the calculation are presented in Fig. 3 for the input φ_0^2 and φ_0^4 to Eq. (11). We assumed that $\Gamma_p / \gamma = 10/3$, $\omega_b = 0$ and $\Gamma = 10^2 \gamma$. It was

found that in view of the structure of the system of equations, the solution for $f_Q^{K < 2}$ already converges, if we account for the PM with $K, x < 6$ in Eq. (7). In view of the properties of Clebsch-Gordan coefficients, only the $f_Q^{K < 2}$ affect the intensity of the light [Eq. (9)], therefore, the system falls off, assuming $\varphi_1^x \gg 8 = 0$. Also the corresponding relative values of the PM of the upper state as a function of ω_a / γ are presented in Fig. 3, which demonstrate the Hanle effect of the ground state a . It is obvious that the values entering into the numerator of Eq. (10), $\operatorname{Re} f_2^2 / f_0^2$, begin to exceed the classical limit of weak excitation with increasing ω_a / γ , at the same time as the values of f_0^2 / f_0^2 entering into the denominator remain less than this limit for weak excitation. This also causes the degree of polarization to exceed the limit value of 1/7.

If we determine, as is sometimes done,⁴ the degree of polarization P_{Σ} relative to the overall intensity of fluorescence

$$P_{\Sigma} = \frac{I_x - I_y}{I_x + I_y + I_z}, \quad (12)$$

then P_{Σ} turns out to be directly proportional to $\operatorname{Re} f_2^2 / f_0^2$ and is not associated with the longitudinal detuning f_0^2 . For P and R transitions

$$P_{\Sigma}^{(P, R)} = \frac{\sqrt{6}}{3} \operatorname{Re} f_2^3 / f_0^3. \quad (13)$$

The corresponding expression in terms of φ_0^2 and φ_0^4 has the form

$$P_{\Sigma}^{(P, R)} (\omega_a / \tau \gg 1, \omega_b / \Gamma \ll 1) = \frac{7 - 10\varphi_2^3 / \varphi_0^3 + 3\varphi_4^3 / \varphi_0^3}{70 + 35\varphi_2^3 / \varphi_0^3} \quad (14)$$

and exceeds the limit of weak excitation, equal to 1/10.

We will now determine, whether or not the Hanle effect of the ground state always causes the degree of polarization to exceed its weak excitation limit. For comparison we will consider a Q type transition.

The degree of polarization $P^{(Q)}$ is expressed in terms of the PM of the excited state as

$$P^{(Q)} = \frac{-\sqrt{6} \operatorname{Re} f_2^3 / f_0^3}{1 - f_2^3 / f_0^3}. \quad (15)$$

For $\omega_a / \gamma \gg 1$ and $\omega_b / \Gamma \ll 1$, the expression in terms of PM of the ground state has the form

$$P^{(Q)} (\omega_a / \tau \gg 1, \omega_b / \Gamma \ll 1) = \frac{7 - 10\varphi_2^3 / \varphi_0^3 + 3\varphi_4^3 / \varphi_0^3}{14 - 20\varphi_2^3 / \varphi_0^3 + 6\varphi_4^3 / \varphi_0^3} = \frac{1}{2}, \quad (16)$$

i.e., the Hanle effect of the lower level is independent of the nonlinearity parameter Γ_p / γ , the degree of polarization is restored to an accuracy of 1/2, which coincides with the limit of weak excitation. Such a result is completely understandable in the classical model. Actually the precession about H of the angular momenta J_a and of the dipole moments \mathbf{p} of the transition, parallel to them, eliminates the anisotropy of the distribution \mathbf{p} in the XY plane [Fig. 2(a)], and this, when determining the degree of polarization, in accordance with Eq. (4), is equivalent to excitation of an ensemble of particles with isotropically distributed angular momenta.

The variation in PM and $P^{(Q)}$ with an increase in ω_a / γ

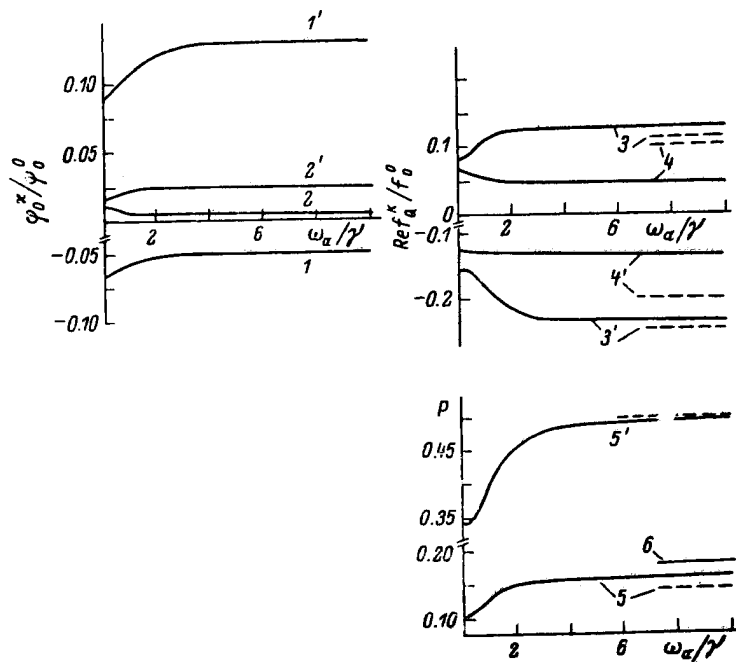


FIG. 3. Calculated dependences on the parameter ω_a/γ for polarized moments (PM) of the ground state φ_0^2/φ_0^0 (1—P, R; 1'—Q transition) and φ_0^4/φ_0^0 (2—P, R; 2'—Q transition), for PM of the excited state $\text{Re} f_2^2/f_0^2$ (3—P, R; 3'—Q transition) and f_0^2/f_0^0 (4—P, R; 4'—Q transition), for the degree of polarization P (5—P, R; 5'—Q transition). Line 6 denotes the maximum possible P value for P and R transitions. The dashed line denotes the corresponding values in the limit of weak light excitation.

is shown in Fig. 3 (curves 1'–5'). It is obvious that singly the values $\text{Re} f_2^2/f_0^2$ and f_0^2/f_0^0 (in contrast to the case of P and R transitions), in absolute value, remain less than the linear limit. Their behavior, of course, is governed by the variable dependence of φ_0^2/φ_0^0 and ω_a/τ , compare curves 1', 2' and 1, 2.

However, if we use the definition of the degree of polarization from Eq. (12), then $P_{\Sigma}^{(Q)} = (-2\sqrt{6}/3)\text{Re} f_2^2/f_0^2$, and as curve 3 of Fig. 3 indicates, the values of $P_{\Sigma}^{(Q)}$ ($\omega_a/\tau \gg 1$, $\omega_b/\Gamma \ll 1$) remain less than the linear limit of $2/5$. The relation between $P_{\Sigma}^{(Q)}$ and φ_0^2 has the form

$$P_{\Sigma}^{(Q)} (\omega_a/\tau \gg 1, \omega_b/\Gamma \ll 1) = \frac{14 - 20\varphi_0^2/\varphi_0^0 + 6\varphi_0^4/\varphi_0^0}{35(1 - \varphi_0^2/\varphi_0^0)}. \quad (17)$$

So, only in the case of P and R transitions, in a situation where the Hanle effect for an optically detuned ground state has already come into play, via destruction, and for an excited state where the effect has not yet developed, do the values for the degree of polarization exceed the weak excitation limit, equal to $1/7$. This results in the unique simultaneous action of precession of the detuned angular momenta of the ground state \mathbf{J}_a about the magnetic field \mathbf{H} and rotation of the dipole moments \mathbf{p} about \mathbf{J}_a . For the case of Q transitions, where there is no rotation of \mathbf{p} about \mathbf{J}_a since $\mathbf{p} \parallel \mathbf{J}_a$, the degree of polarization does not exceed the limit of weak excitation. But since the anisotropy of the distribution of angular momenta \mathbf{J}_a remains, the agreement between the values of the degree of polarization for $\omega_a/\tau \gg 1$ and those in the limit

of weak excitation, equal to $1/2$, should be considered exceptional. This is confirmed by the fact that under such conditions, the degree of polarization $P_{\Sigma}^{(Q)}$, defined according to Eq. (12), remains less than its own limiting value of $2/5$, under weak excitation.

¹W. Hanle, Z. Phys. 30, 93 (1924).

²P. P. Feofilov, *The Physical Basis of Polarized Emission* (Moscow, 1959); Consultants, Bur., New York, 1961).

³W. Happer, Rev. Mod. Phys. 44, 169 (1972).

⁴M. P. Chaika, *Interference of Degenerate Atomic States* (Leningrad, 1975).

⁵R. E. Drullinger and R. N. Zare, J. Chem. Phys. 51, 5532 (1969); 59, 4225 (1973).

⁶R. S. Ferber, Izv. Akad. Nauk Latv. SSR 8, 85 (1978).

⁷M. Ducloy, J. Phys. B 9, 357 (1976).

⁸M. Ya. Tamanis, R. S. Ferber, and O. A. Shmit, in *Theoretical Spectroscopy* (1977), p. 17.

⁹R. S. Ferber, O. A. Shmit, and M. Ya. Tamanis, Chem. Phys. Lett. 61, 441 (1979).

¹⁰M. Ya. Tamanis, R. S. Ferber, and O. A. Shmit, Opt. Spektrosk. 53, 755 (1982) [Opt. Spectrosc. (USSR) 53, 449 (1982)].

¹¹M. P. Auzin'sh and R. S. Ferber, Opt. Spektrosk. 55, 1105 (1983) [Opt. Spectrosc. (USSR) 55, 674 (1983)].

¹²E. N. Kotlikov and V. A. Kondratova, Opt. Spektrosk. 48, 667 (1981) [Opt. Spectrosc. (USSR) 48, 367 (1981)].

¹³M. I. Dyakonov, Zh. Eksp. Teor. Fiz. 47, 2229 (1964) [Sov. Phys. JETP. 20, 494 (1964)].

¹⁴R. S. Ferber, A. I. Okunevich, O. A. Shmit, and M. Ya. Tamanis, Chem. Phys. Lett. 90, 476 (1982).

¹⁵M. P. Auzinsh, Izv. Akad. Nauk Latv. SSR Ser. Fiz. i Tekh. Nauk 1, 9 (1984).