Polarization of laser-excited fluorescence of diatomic molecules and the magnetic-field effect

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(Received 5 November 1986)
Opt. Spektrosk. 63, 1220–1226 (December 1987)

The degree of linear polarization of laser-induced fluorescence under optical pumping of diatomic molecules is studied theoretically as a function of the type of molecular transition, the magnitude of the angular momenta of the states associated with optical transition, and the rate of absorption of laser light without and with a magnetic field. The repolarizing effect of the magnetic field is studied in the case of the Hanle effect of the ground state. Analytical expressions are derived for the dependence of the degree of polarization of fluorescence on the angular momentum of the molecules under optical pumping without a magnetic field.

Let us study the degree of polarization of laser-induced fluorescence (LIF) as a result of linearly polarized excitation of diatomic molecules from the vibrational–rotational (VR) level v'', J'' of the electronic ground state α'' to the VR level v', J' of the excited electronic state α' (Fig. 1). In the case, when the rate of absorption of light Γ_p is much less than the rate of relaxation both in the ground state γ_x, and in the excited state Γ_k, the degree of polarization of LIF in the $(\alpha',v',J') \to (\alpha'',v_1'',J_1'')$ transition for different types of molecular transitions has been studied for a long time.[1] In this

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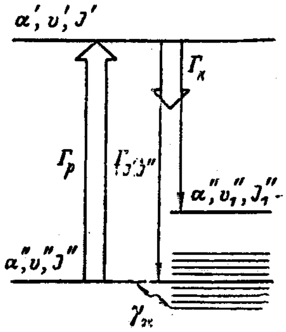

FIG. 1. Optical pumping scheme of diatomic molecules.

case, depolarization of the radiation or the Hanle effect[2] is observed on imposition of a transverse magnetic field. The Hanle signal is often found to be very broad for the excited dimer levels. Its halfwidth is equal to several tesla in a number of cases.[3]

If the rate of absorption of light cannot be taken to be small ($\Gamma_p \gtrsim \gamma_\varkappa$), then optical pumping of diatomic molecules gives rise to destruction.[4] When observing fluorescence in a direction orthogonal to the direction of excitation and the E vector of the exciting light, optical pumping leads to noticeable reduction in the degree of polarization of the radiation. Its dependence on the pumping parameter $\chi = \Gamma_p/\gamma_\varkappa$ and angular momentum J', J'', and J_1'' is studied theoretically for $Q\uparrow Q\downarrow (J''\to J' = J''\to J_1'' = J'')$ type transitions in Ref. 4, and for $P\uparrow R\downarrow$ $(J''\to J' = J'' - 1 \to J_1'' = J'' - 2)$ and $P\uparrow P\downarrow$ $(J''\to J' = J'' - 1\to J_1'' = J'')$ types in Ref. 5. Dependence of the degree of polarization of the LIF on χ under optical pumping of dimers can be found in Refs. 4, 6, and 7 in the classical limit of large angular momenta for different types of molecular transitions.

Imposition of a transverse magnetic field on the optically pumped ensemble of molecules leads to simultaneous appearance of the Hanle effect in the LIF of both the ground and excited levels. The Hanle signal of the ground state for many dimers is found to be much narrower than the signal from the excited level.[3] In this case, the magnetic field first increases the degree of polarization of LIF—the Hanle effect of the lower level, and with further increase in the field, depolarization of LIF is observed, when the Hanle effect of the excited level enters. In the limit of large angular momenta, it is well known that the degree of polarization of LIF for the P and R transitions, unlike the Q transition, can exceed the value under weak excitation without the magnetic field,[7] as a result of reorienting action of the magnetic field. Such a phenomenon is recorded experimentally in Te_2 molecules in Ref. 8.

However, up to now, the reorienting action of the magnetic field in the case of the Hanle effect of the ground state for levels with arbitrary angular momentum has not been investigated. Dependence of the degree of polarization of LIF on angular momentum and the parameter χ under optical pumping without a magnetic field has also not been studied for a number of molecular types of transitions. This paper is devoted to the clarification of these important questions for practical application of diatomic molecules.

We will study the dependence of the degree of polarization of LIF on the external magnetic field and angular momenta of the levels under optical pumping in a polarization-moment (PM) apparatus.[2] We write the equations relating PM of the excited state f_Q^K and the ground state $\varphi_q^\varkappa$ (Ref. 9) on the form proposed in Ref. 10,

$$\Gamma_p \sum_{X\varkappa} {}^K F^{X\varkappa} \{\Phi^{(X)} \otimes \varphi^{(\varkappa)}\}_Q^K - \Gamma_p \left(\frac{\Pi_{J'}}{\Pi_{J''}}\right)^2$$

$$\times \sum_{XK'} {}^K A_1^{XK'} \{\Phi^{(X)} \otimes f^{(K')}\}_Q^K - (\Gamma_K - iQ\Omega) f_Q^K = 0, \tag{1a}$$

$$-\Gamma_p \sum_{X\varkappa'} {}^\varkappa A^{X\varkappa'} \{\Phi^{(X)} \otimes \varphi^{(\varkappa')}\}_q^\varkappa$$

$$+\Gamma_p \left(\frac{\Pi_{J'}}{\Pi_{J''}}\right)^2 \sum_{XK} {}^\varkappa F_1^{XK} \{\Phi^{(X)} \otimes f^{(K)}\}_q^\varkappa - (\gamma_\varkappa - iq\omega)\varphi_q^\varkappa +$$

$$+\Gamma_{J'J''} C_\varkappa \delta_{K\varkappa}\delta_{Qq} f_Q^K + \lambda_q^\varkappa \delta_{\varkappa 0}\delta_{q0} = 0, \tag{1b}$$

where the coefficients

$${}^\varkappa A^{X\varkappa'} = \frac{[1 + (-1)^{\varkappa + X + \varkappa'}]}{2}$$

$$\times \frac{\Pi^2_{J'X\varkappa'}}{\Pi_\varkappa} (-1)^{J' - J'' + \varkappa'} \begin{Bmatrix} \varkappa & X & \varkappa' \\ J'' & J'' & J'' \end{Bmatrix} \begin{Bmatrix} 1 & 1 & X \\ J'' & J'' & J' \end{Bmatrix}, \tag{2a}$$

$${}^K F^{X\varkappa} = \frac{\Pi^3_{J'} \Pi^2_{X\varkappa}}{\Pi_{J''K}} (-1)^{X+1} \begin{Bmatrix} K & J' & J' \\ X & 1 & 1 \\ \varkappa & J'' & J'' \end{Bmatrix}, \tag{2b}$$

$$C_\varkappa = (-1)^{J' - J'' + \varkappa + 1} \Pi^{J''J'} \begin{Bmatrix} J'' & J'' & \varkappa \\ J' & J' & 1 \end{Bmatrix}, \tag{2c}$$

while $\Pi_{ab\ldots} = \sqrt{(2a+1)(2b+1)\ldots}$, and $\begin{Bmatrix} \cdots \\ \cdots \\ \cdots \end{Bmatrix}$ and $\begin{Bmatrix} \cdots \\ \cdots \end{Bmatrix}$ are the $9j$ and $6j$ symbols. The frequencies $\omega = g''\mu_B H/\hbar$ and $\Omega = g'\mu_B H/\hbar$ characterize magnetic splitting of the ground state with Lande factor g'' and the excited state with Lande factor g', μ_B is the Bohr magneton, H is the external magnetic field intensity. The constant $\lambda_q^\varkappa \delta_{\varkappa 0}\delta_{q0}$ is the rate of isotropic restoration of the population of the lower level by interaction with the thermostat, in which particles not subjected to laser excitation play a role. ${}^K A_1^{XK'}$ and ${}^\varkappa F_1^{XK}$ differ from ${}^\varkappa A^{X\varkappa'}$ and ${}^K F^{X\varkappa}$ in the fact that the first characterize stimulated emission, and in them J' and J'' exchange places, as compared to the second pair, characterizing light absorption.

The tensor $\Phi^{(X)}$ depicts polarization of the exciting light,[2] $\Gamma_{J'J''}$ is the rate of reverse spontaneous transitions. The maximum possible value of the rank of PM in Eqs. (1a) and (1b) is determined by the angular momentum of the transitions: $0 \leqslant K \leqslant 2J'$, $0 \leqslant \varkappa \leqslant 2J''$.

The intensity of LIF in the transition $(\alpha', v', J') \to (\alpha'', v_1'', J_1'')$ (Fig. 1) is determined by the $f_Q^{K\leqslant 2}$ of the PM and can be calculated from the formula of Ref. 2.

$$I = I_0 (-1)^{J'+J_1''} \sum_K \Pi_K^2 \begin{Bmatrix} 1 & 1 & K \\ J' & J' & J_1'' \end{Bmatrix} \sum_Q (-1)^Q f_Q^K \Phi_{-Q}^K. \tag{3}$$

For computer solution of the set of Eqs. (1a) and (1b) with arbitrary values of the dynamic constants and angular momenta J_1 and J'', it is convenient to study the symmetry properties of the coefficients ${}^{\varkappa}A^{X\varkappa'}$ and ${}^{\varkappa}F^{XK}$ (these properties are considered in Ref. 11 for the asymptotic limit of large angular momenta). We can show that for P, Q, and R types of molecular transitions

$${}^{\varkappa_1}A^{X\varkappa_2} = {}^{\varkappa_2}A^{X\varkappa_1} \left(\frac{\Pi_{\varkappa_2}}{\Pi_{\varkappa_1}}\right)^3 (-1)^{\varkappa_1+\varkappa_2}. \tag{4}$$

This property is, of course, also valid for ${}^{K_1}A_1^{XK_2}$. For the coefficients ${}^{K}F^{X\varkappa}$ and ${}^{\varkappa}F_1^{XK}$

$${}^{K}F^{X\varkappa} = {}^{\varkappa}F^{XK} \left(\frac{\Pi_K}{\Pi_\varkappa}\right)^3 C, \tag{5}$$

where $C = 1$ for the Q transition, and for the P transition

$$C = \left[\frac{(2J'+3+\varkappa)!\,(2J'+2-\varkappa)!\,(2J'+1+\varkappa)!\,(2J'-\varkappa)!\,(2K+1)!}{(2J'+1+K)!\,(2J'-K)!\,(2\varkappa+1)!\,(2J'+3+K)!\,(2J'+2-K)!}\right]^{1/2} (-1)^X \frac{\Pi_\varkappa}{\Pi_K}. \tag{6}$$

We can obtain the coefficient C in the case of R transition from Eq. (6) by exchanging the places of K and $\varkappa$ and replacing J' by J''. Nevertheless, when the symmetry properties obtained are used, the complete set of Eqs. (1a) and (1b) for J of the order of a few tens cannot be solved even on comparatively large computers. However, since only the LIF intensity I is of most interest, which is determined by the $f_Q^{K\leq 2}$ of PM [see Eq. (3)], it seems possible to truncate the set of Eqs. (1a) and (1b) for large J for K, $\varkappa$ larger than some value $K_{max} < 2J'$ and $\varkappa_{max} < 2J''$. Verification showed that even for comparatively large values of the parameters $\Gamma_p/\gamma_\varkappa$, $\Gamma_p/\Gamma_K \sim 10$, solution for the LIF intensity converges rapidly with increasing K_{max} and $\varkappa_{max}$. In performing all the calculations, the results of which are given in this paper, this convergence has been specifically checked. In these calculations, not once did the necessity arise to include PM of rank higher than 10.

Calculation for the dependence of the degree of polar-

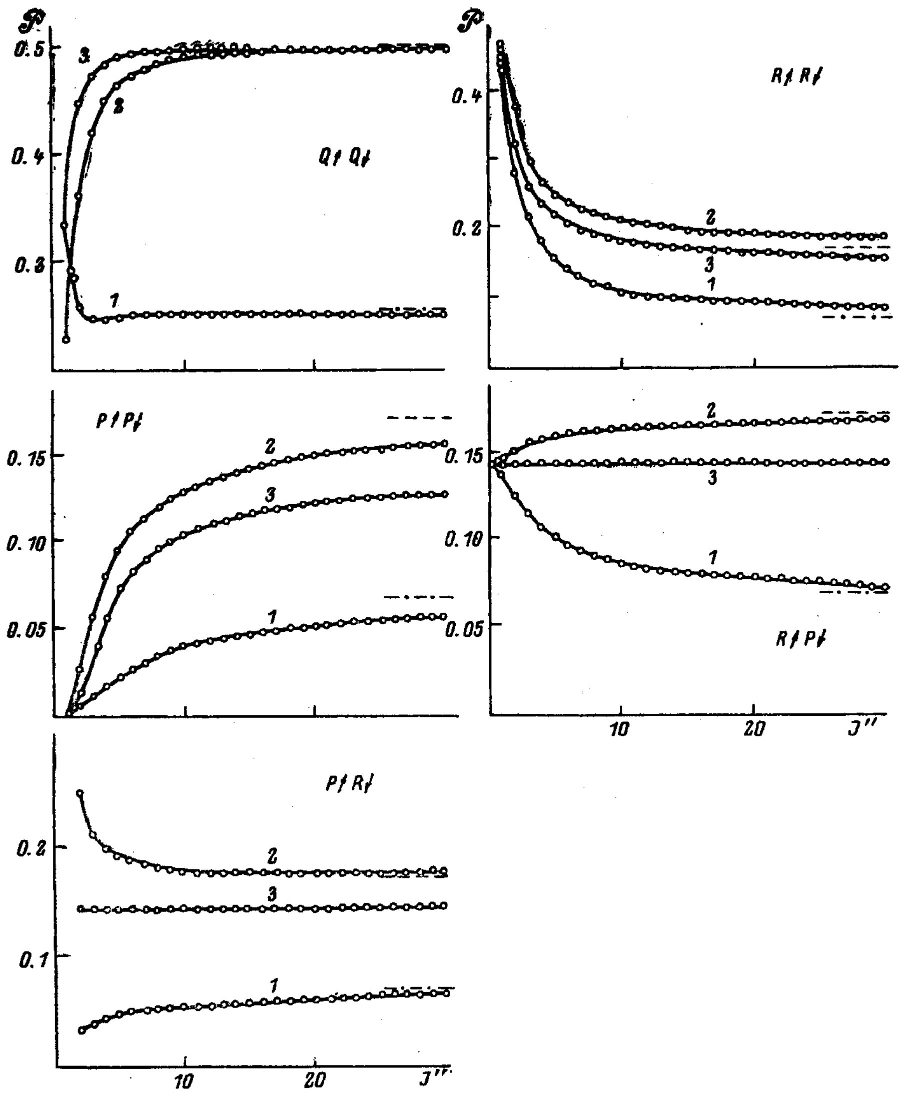

FIG. 2. Degree of polarization of LIF vs the angular momentum J'' for different types of molecular transitions. 1—for the situation $\omega/\gamma_\varkappa \ll 1$, $\Omega/\Gamma_K \ll 1$. 2—for the situation $\omega/\gamma_\varkappa \gg 1$, $\Omega/\Gamma_K \ll 1$, 3—for the situation of weak excitation (computed according to Ref. 1).

ization of the LIF on J'' and χ was made for two situations, when $\omega/\gamma_x \ll 1$, $\Omega/\Gamma_K^{\ll 1}$ and $\omega/\gamma_x \gg 1$, $\Omega/\Gamma_K \ll 1$. The first case means the absence of the magnetic field, and the second, it is realized in the range of magnetic fields where the Hanle effect of the ground state was complete, and that of the excited state did not begin to appear, i.e., that range where excess of the degree of polarization of the LIF over the limiting value under weak field excitation[7] is observed in the asymptotic limit of large J. The $\mathscr{P}(J'')$ curves obtained are shown in Fig. 2 for the following values of the dynamic constants: $\gamma = \gamma_x = 0.3\ \mu\text{sec}^{-1}$, $\Gamma_K = \Gamma = 10^4\ \mu\text{sec}^{-1}$, $\Gamma_{J'J''} = 0$, $\chi = \Gamma_p/\gamma = 10$. The values of the constants are chosen so as to eliminate the effect of stimulated and reverse spontaneous transitions. On the one hand, this was done with the purpose that the results obtained be dependent possibly on fewer parameters. On the other hand, the values of the constants used for not too small J approximated the actual situation of a number of dimers.[3] It is clear from Fig. 2 that in the case $\varphi/\gamma_x \gg 1$, $\Omega/\Gamma_K \ll 1$ for the P and R transitions for any J'' values, the degree of polarization is greater than the limiting weak excitation value. Furthermore, this excess for RR, RP, and PP transition increases with increasing J'', and an inverse dependence is observed for the PR transitions. In the limit of large J'', in all cases when $\omega/\gamma_x \gg 1$, $\Omega/\Gamma_K \ll 1$, the degree of polarization for the P and R transitions has the same limit[6,7] for chosen values of the parameters, and is equal to $\mathscr{P}(\omega/\gamma_x \gg 1, \Omega/\Gamma_K \ll 1, J'' \to \infty) = 0.1698$ (it is shown as a dashed line in Fig. 2). For QQ transition, the degree of polarization of LIF for small J'' is smaller than the weak excitation limit and reaches this limit only for large J''. It is interesting to note that the asymptotic limit of the degree of polarization for RP, PR, and QQ transitions (curves *1,2*) is already reached for $J'' \sim 20$, and the convergence PP and RR transitions is much worse and the asymptote is reached only when $J'' \sim 100$. The asymptotic limit for the degree of polarization $\mathscr{P}(\omega/\gamma_x \ll 1, \Omega/\Gamma_K \ll 1, J'' \to \infty)$, equal to 0.0680 for the P and R transitions is calculated according to Refs. 6, 7 and is shown in Fig. 2 as the dot–dash line. We must note that the amplitude of the Hanle effect of the lower state (the distance between curves *2* and *1* in Fig. 2) for the PP, RR, RP, and QQ transitions is maximum when $J'' \to \infty$, and at small J'' values for the PR type. It is interesting that for $J'' = 1$ and QQ transition, it even changes sign. This means that the Hanle effect of the ground state does not lead to an increase in the degree of polarization, but on the contrary, to a reduction.

Analytical expressions are also derived for the curves *1* in Fig. 2. Calculation is done based on the Heisenberg spectroscopic stability principle by the technique of Refs. 1 and 4. This is done there for the QQ transitions. The essence of the method is as follows: If the quantization axis is chosen to be along the E vector of the exciting light, then the probability of absorption is proportional to the square of the Clebsch-Gordan coefficient $W \sim (C^{J'M}_{J''M10})^2$. The luminescence probability of light polarized parallel to E is proportional to $W_\parallel \sim (C^{J'M}_{J_1''M10})^2$, while that polarized perpendicular to E is proportional to $W_\perp \sim 1/2[(C^{J'M}_{J_1''M+11-1})^2 + (C^{J'M}_{J_1''M-111})^2]$, where M is the magnetic quantum number. Then, the intensity of light of the two polarizations is

$$I_\parallel \sim \sum_M n_M \left(C^{J'M}_{J''M10}\right)^2 \left(C^{J'M}_{J_1''M10}\right)^2, \tag{7a}$$

$$I_\perp \sim \frac{1}{2} \sum_M n_M \left(C^{J'M}_{J''M10}\right)^2 \left[\left(C^{J'M}_{J_1''M+11-1}\right)^2 + \left(C^{J'M}_{J_1''M-111}\right)^2\right], \tag{7b}$$

where n_M is the population of the magnetic sublevel of the ground state, which is in the case of optical pumping[4]

$$n_M = \frac{n_0}{1 + \chi\left(C^{J'M}_{J''M10}\right)^2}. \tag{8}$$

Using Eqs. (7a), (7b), and (8), we find the degree of polarization of fluorescence for P and R transitions with magnetic field and with optical pumping

$$\mathscr{P}_{PR} = \left(\sum_M \frac{(J^2 - M^2)(J^2 - 3M^2 - J)}{1 + \chi(J^2 - M^2)/(2J^2 + J)}\right) \Bigg/ \left(\sum_M \frac{(J^2 - M^2)[-M^2 + (3J - 4)(J - 1)]}{1 + \chi(J^2 - M^2)/(2J^2 + J)}\right), \tag{9}$$

$$\mathscr{P}_{PP} = \left(\sum_M \frac{(J^2 - M^2)(J^2 - 3M^2 - J)}{1 + \chi(J^2 - M^2)/(2J^2 + J)}\right) \Bigg/ \left(\sum_M \frac{(J^2 - M^2)(3J^2 - M^2 + J)}{1 + \chi(J^2 - M^2)/(2J^2 + J)}\right), \tag{10}$$

$$\mathscr{P}_{RR} = \left(\sum_M \frac{[(J+1)^2 - M^2](J^2 + 3J - 3M^2 + 2)}{1 + \chi[(J+1)^2 - M^2]/[(J+1)(2J+1)]}\right) \Bigg/ \left(\sum_M \frac{[(J+1)^2 - M^2](3J^2 + 5J - M^2 + 2)}{1 + \chi[(J+1)^2 - M^2]/[(J+1)(2J+1)]}\right), \tag{11}$$

$$\mathscr{P}_{RP} = \left(\sum_M \frac{[(J+1)^2 - M^2](J^2 + 3J - 3M^2 + 2)}{1 + \chi[(J+1)^2 - M^2]/[(J+1)(2J+1)]}\right) \Bigg/ \left(\sum_M \frac{[(J+1)^2 - M^2](3J^2 + 13J - M^2 + 14)}{1 + \chi[(J+1)^2 - M^2]/[(J+1)(2J+1)]}\right). \tag{12}$$

We should understand J to be J'' in Eqs. (9)–(12). Equations (9) and (10) are also derived in Ref. 5. Unfortunately, there is error in both formulas in this paper.

Dependence of the degree of polarization of LIF on the pumping parameter χ for angular momentum $J'' < 5$, calculated according to Eqs. (1a) and (1b), is given in Fig. 3, i.e., for the situation, when Eqs. (1a) and (1b) can be solved on the computer, taking into account all PM generated. For $J'' = 1$ and QQ transitions, we would also be able to solve these equations analytically when $\omega/\gamma_x \gg 1$, $\Omega/\Gamma_K \ll 1$. In this case, the degree of polarization of LIF is related to the PM of the ground state by

$$\mathscr{P} = \frac{1}{3}\left(1 - \sqrt{10}\,\frac{\varphi_0^2}{\varphi_0^0}\right). \tag{13}$$

By expressing $\varphi_q^\varkappa$ in terms of χ, we obtain

$$\mathscr{P} = \frac{1}{3} - \frac{48\chi + 52\chi^2 + 18\chi^3 + 2\chi^4}{864 + 1296\chi + 714\chi^2 + 171\chi^3 + 15\chi^4}. \tag{14}$$

The fact that the degree of polarization of LIF without magnetic field for the PP and PR transitions tends to zero with increasing χ, while the same tendency appears only when $J'' \to \infty$ for the QQ, RR, and RP transitions is interesting. Using Eqs. (11) and (12) we can obtain for the limit of $\mathscr{P}$ as $\chi \to \infty$ as a function of J'' for the RR and RP types of transitions

$$\mathscr{P}_{RR}(\chi \to \infty) = \frac{3(J+1)}{4J^2 + 7J + 3}, \tag{15}$$

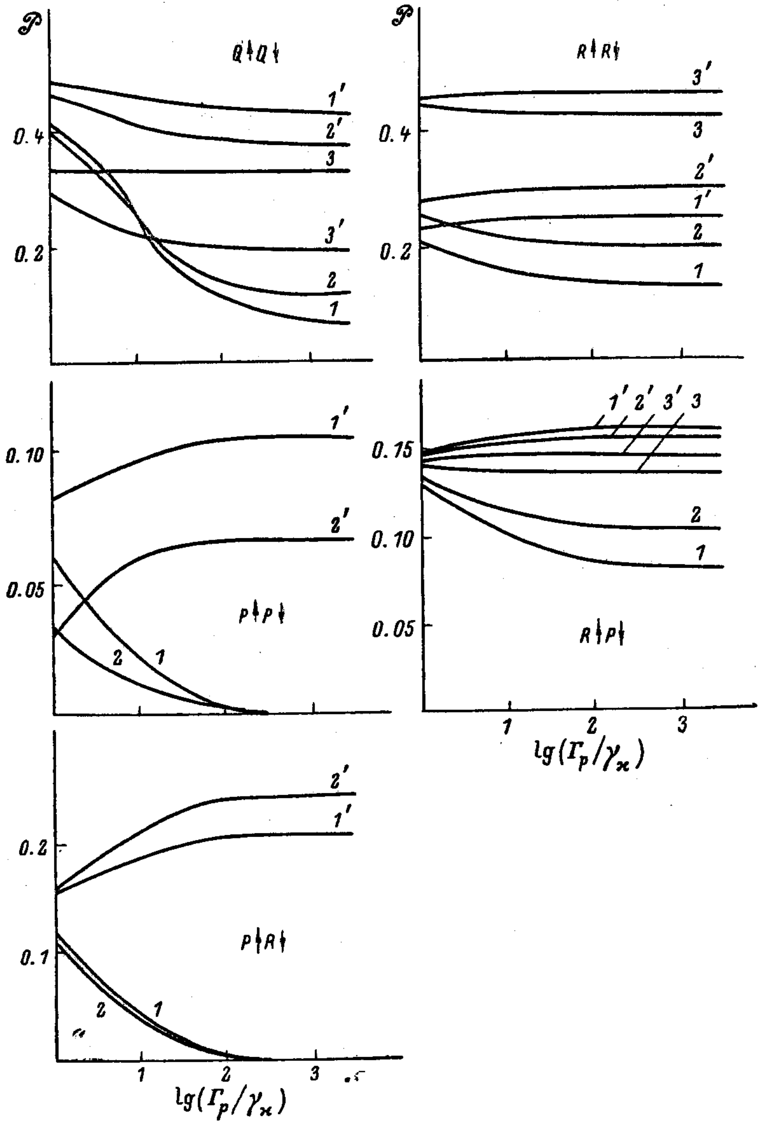

FIG. 3. Degree of polarization of LIF vs the pumping parameter $\chi = \Gamma_p/\gamma_\kappa$ for various types of molecular transitions. For the situation $\omega/\gamma_\kappa \ll 1$, $\Omega/\Gamma_K \ll 1$; J'': *1*—5, *2*—3, *3*—1. For the situation $\omega/\gamma_\kappa \gg 1$, $\Omega/\Gamma_K \ll 1$; J'': *1'*—5, *2'*—3, *3'*—1.

$$\mathscr{P}_{RP}(\chi \to \infty) = \frac{3(J+1)}{4J^2+19J+21}\,. \tag{16}$$

We note that for the *PP* and *RP* transitions as $\chi \to \infty$ and $J'' \sim 1$, the polarization of LIF does not reach the limiting value of 0.1781 (Ref. 7) as $J'' \to \infty$, while it exceeds it for the *RR* and *PR* transitions. The polarization of LIF for the *QQ* transitions as $\chi \to \infty$ and $J'' \sim 1$ is less than the limiting value of 0.5 (Ref. 7) reached at large angular momenta for the case $\omega/\gamma_\kappa \gg 1$, $\Omega/\Gamma_K \ll 1$.

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