Optical orientation and alignment of high-lying vibrational–rotational levels of diatomic molecules under their fluorescence population

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The possibilities of producing optical orientation and alignment in high-lying (thermally unpopulated) vibrational–rotational (VR) levels of the ground electronic state of diatomic molecules through populating them in spontaneous emission are considered. In this work a description and numerical modeling of the anticipated signals in fluorescence excited from high-lying levels by a probing beam in the presence of an external magnetic field (the Hanle effect and quantum beats in the kinetics of the transition process) are presented. The different types of transitions and states of polarization of the radiation are considered. An estimate of the attainable population of high-lying VR levels through fluorescence for alkali dimers in gases is made.

INTRODUCTION

Let radiation give rise to the electronic–vibrational–rotational (EVR) transition ($J'' \to J'$) in a diatomic molecule with resolved vibrational–rotational (VR) structure (Fig. 1). If $\Gamma_P/\lambda \gtrsim 1$, where Γ_P is the absorption rate, τ is the rate of nonradiative relaxation in the system of VR levels of the ground term a'', then optical alignment and orientation[1,2] of the level J'' by emptying can be produced; and the Hanle effect[3] and quantum beats[4,5] are observed. At the same time another form of optical pumping by populating is possible: during emission of the resonance fluorescence series from the level J' of the excited term a' high-lying levels of VR levels of the state a'' are populated. One such transition $J' \to J_1''$ with rate $\Gamma_{J'J_1''}$ is shown in Fig. 1: The value of $\Gamma_{J'J''}$ depends on the Franck-Condon factor and the strength of the electronic transition.[10] In the spontaneous process to the level J_1'' polarization moments (PM) are transferred from the upper level: population ${}_1\varphi_0^0$, orientation ${}_1\varphi_q^1$, alignment ${}_1\varphi_q^2$ and others.[11] The high-lying VR levels v_1'', J_1'' turn out to be optically aligned or oriented, whereupon the lifetime $\tau_1 = {}_1\gamma_\varkappa^{-1}$ is determined by the relaxation rate ${}_1\gamma_\varkappa$ of the corresponding PM. In the general case ${}_1\gamma_\varkappa \approx \gamma_\varkappa$ this time must exceed the lifetime during optical pumping emptying, because the latter is the order of $(\gamma_\varkappa + \Gamma_P)^{-1}$. Characteristics of the radiation (intensity, polarization) in the cycle $J_1'' \to J_1' \to J_2''$ (the dashed lines of Fig. 1) contain data about the relaxation and magnetic constants of the levels J_1'', which is important for modeling processes in gaseous lasers and diatomic molecules.[12] Research is underway for the possibilities of applying new methods, for example SRS spectroscopy, to homonuclear molecules.[13]

The present work is devoted to describing and numerically modeling the anticipated signals during optical pumping by populating both for the steady-state and pulsed excitation in the presence of an external magnetic field (the Hanle effect and quantum beats). An estimate is given of the magnitudes of the signals under actual experimental conditions for alkali dimers.

KINETIC EQUATIONS

During excitation let the approximation of broad line excitation (BLA) be satisfied.[14] We write the equation of motion of the PM ${}_1\varphi_q^\varkappa$ of levels J_1'', taking into account the fact that $J'', J' \gg 1$,[15] in the following form[4]

$$-({}_1\gamma_\varkappa - iq\omega_1)\,{}_1\varphi_q^\varkappa + \Gamma_{J'J_1''} f_Q^K \delta_{K\varkappa}\delta_{Qq} = {}_1\dot{\varphi}_q^\varkappa. \quad (1)$$

Here ω_1 is the frequency of the Zeeman splitting of the J_1'' level, and the term with $\Gamma_{J'J_1''}$ describes its population by spontaneous transitions in the cycle $\varphi_q^\varkappa \xrightarrow{\Gamma_P} f_Q^K \xrightarrow{\Gamma_{J'J_1''}} {}_1\varphi_q^\varkappa$. It is assumed that nonradiative relaxation does not lead to populating the J_1'' state, because it is sufficiently highly excited and in the limits of kT it is surrounded thermally by unpopulated VR levels. The steady-state solution of Eq. (1) is

$$ {}_1\varphi_q^\varkappa = f_q^\varkappa \Gamma_{J'J_1''} / ({}_1\gamma_\varkappa - iq\omega_1). \quad (2)$$

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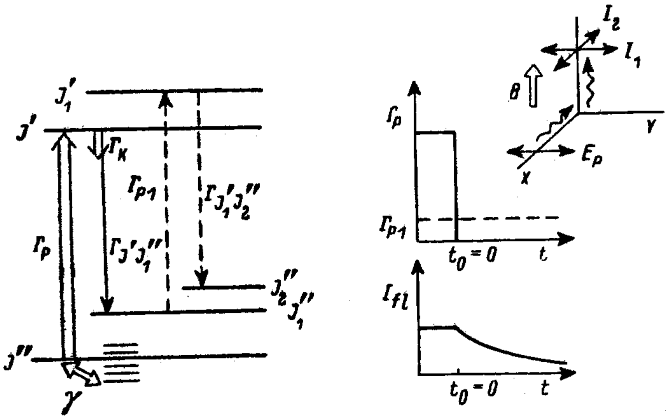

FIG. 1. Scheme of the construction and recording of optical pumping for fluorescence populating. On the right is shown the geometry of the experiment, excitation, and recording of the kinetics of the transition process.

We determine the PM of the excited level $f_q^{\varkappa}$ entering in Eq. (2) from[11,15]

$$-(\Gamma_K - iQ\Omega) f_Q^K + F_Q^K = 0, \tag{3}$$

in which the pumping tensor can be written (without considering the induced transitions $\Gamma_P \ll \Gamma_K$) by $\varphi_q^{\varkappa}$ (Ref. 5)

$$F_Q^K = \Gamma_P \sum_{\varkappa q} {}_Q^K D_q^{\varkappa} \varphi_q^{\varkappa},$$

$${}_Q^K D_q^{\varkappa} = (-1)^{\Delta} \sqrt{\frac{2\varkappa+1}{2K+1}} \sum_X \sqrt{2X+1}\, C_{1\Delta 1-\Delta}^{X0} C_{X0K0}^{\varkappa 0} C_{XQ-q\varkappa q}^{KQ} \Phi_{Q-q}^X(\mathbf{e}). \tag{4}$$

Here $\Phi_{Q-q}^X(\mathbf{e})$ is a function introduced by Dyakonov[11] for the state of polarization of the exciting light e, $C_{a\alpha b\beta}^{c\gamma}$ is a Clebsch-Gordan coefficient, and $\Delta = J' - J''$.

For linearly polarized (LP) excitation the vector $\mathbf{E} \| Z$ (Fig. 1), when $q = 0$, and the degree of alignment $P_{al} = {}_1\varphi_0^2/{}_1\varphi_0^0$; for a Q transition ($J' = J'' = J_1''$) $P_{al}^Q = 2/5$, and for a transition of the P, R type ($J' = J'' \pm 1$, $J_1'' = J' \pm 1$) $P_{al}^{P,R} = -1/5$. For circularly polarized (CP) excitation it is feasible to excite along the Z axis and to speak about the degree of orientation $C_{or} = {}_1\varphi_0^1/{}_1\varphi_0^0$ which for $J', J'' \gg 1$ differs from zero for transitions of the P,R type and equals $C_{or} = \pm 1/2$. Here alignment also arises, the degree of which is 1/10. It is assumed that all the values obtained agree with the corresponding characteristics of the upper level J'.

We compare these values with the quantities attained by optical alignment of the lower level upon emptying it.[1,2] Numerical solutions of the corresponding equations for the PM according to the algorithm described in Ref. 15 give the ratios $\varphi_0^{\varkappa}/\varphi_0^0$ given in Fig. 2. It is evident that PM of high rank $\varkappa > 2$ also appear, for example φ_0^4 and φ_0^6 for LP. From a comparison with the classical description, one is able to obtain the limiting value $\varphi_0^2/\varphi_0^0 = -1/2$ (Q transition) for $\Gamma_P/\gamma \gg 1$, which exceeds the quantity ${}^1\varphi_0^2/{}_1\varphi_0^0 = 2/5$ for pumping by populating but only for very large values of Γ_P/γ (for experimental conditions[1-5] $\Gamma_P/\gamma < 10$ and $|\varphi_0^2/\varphi_0^0| < 0.275$). For P,R-transitions with $\Gamma_P/\gamma \gg 1$ the limit $|\varphi_0^2/\varphi_0^0| = 1$. For CP pumping ($P,R$ transitions) the orientation φ_0^1/φ_0^0 and the alignment coincide and change sign near $\Gamma_P/\gamma = 2$.

We describe the pumping arising in the level J_1'' by means of a probing beam in the cycle ${}_1\varphi_q^{\varkappa} \xrightarrow{\Gamma_{p1}} {}_1f_Q^K \xrightarrow{\Gamma_{J_1'J_2''}} {}_2\varphi_q^{\varkappa}$ (dashed lines in the scheme of Fig. 1). The intensity of the radiation of a given polarization e′ is[15]

$$I(\mathbf{e}') \sim (-1)^{\Delta'} \sum_K \sqrt{2K+1}\, C_{1-\Delta' 1\Delta'}^{K0} \sum_Q (-1)^Q {}_1f_Q^K \Phi_{-Q}^K(\mathbf{e}'), \tag{5}$$

where $\Delta' = J_1' - J_2''$. Here ${}_1f_Q^K$ are also obtained from Eqs. (3) and (4); however, one substitutes the known ${}_1\varphi_q^{\varkappa}$ instead of $\varphi_q^{\varkappa}$ in Eq. (4).

THE HANLE EFFECT

One method of detecting optical alignment or orientation is level crossing in a zero magnetic field or the Hanle effect.[11] We obtain the form of the expected signals by using Eqs. (1)–(5) and assuming identical decay rates of the different PM.

Q transitions, LP excitation. Let the pumping beam $\mathbf{E}_P$ be directed along the X axis and polarized along the Y axis

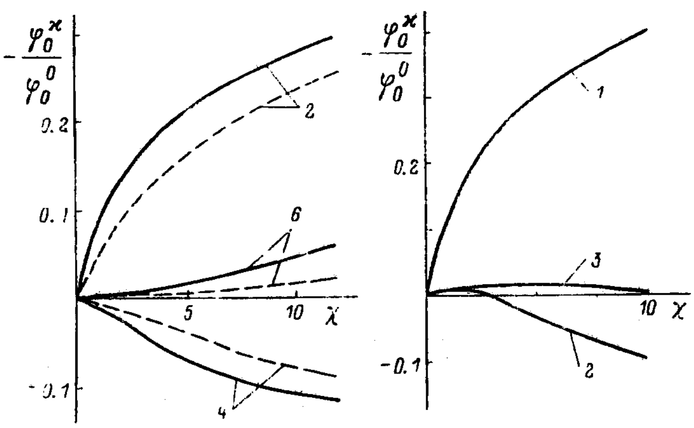

FIG. 2. $\varphi_0^{\varkappa}/\varphi_0^0$ PM rank $\varkappa$ (denoted by numbers) vs $\varkappa = \Gamma_P/\gamma$ for optical emptying of the level J''. On the left is LP pumping (the solid lines are Q excitation, the dashed are P,R excitation), on the right is CP pumping (P,R excitation).

(Fig. 1), the magnetic field $\mathbf{B}\|OZ$, and the probing beam $\mathbf{E}_{P1}$, which produces transitions $J_1''\to J_1'$, be polarized either along $OY(\mathbf{E}_{P1}\|\mathbf{E}_P)$ or along $OX(\mathbf{E}_{P1}\perp\mathbf{E}_P)$. In the second case the probing beam must propagate along the Y or Z axis. The coefficients in Eqs. (3) and (4) equal $F_0^0=\Gamma_P\varphi_0^0/3$, $F_0^2=-\Gamma_P\varphi_0^0/15$, $F_{\pm 2}^2=-\Gamma_P\varphi_0^0/5\sqrt{6}$. The degree of linear polarization of the radiation for the transition $J_1'\to J_2''$, traditionally described by $P=(I_1-I_2)/(I_1+I_2)$ (Fig. 1), is given by the expression

$$P^Q=(\beta_2\pm\beta_3)/(2\tau_1\pm\beta_1), \tag{6}$$

where the $+$ sign corresponds to $\mathbf{E}_{P1}\|\mathbf{E}_P$ and the $-$ sign to $\mathbf{E}_{P1}\perp\mathbf{E}_P$, and

$$\left.\begin{aligned}
\tau_1&=\frac{\Gamma_{P1}\Gamma_P\Gamma_{J'J_1''}}{{}_1\Gamma_1\gamma\Gamma}, \quad \beta_1=\frac{\Gamma_{J'J_1''}\Gamma_{P1}\Gamma_P({}_1\gamma\Gamma-4\omega_1\Omega)}{{}_1\Gamma({}_1\gamma^2+4\omega_1^2)(\Gamma^2+4\Omega^2)},\\
\beta_2&=\frac{\Gamma_{P1}\Gamma_P\Gamma_{J'J_1''}{}_1\Gamma}{\Gamma_1\gamma({}_1\Gamma^2+4\Omega_1^2)},\\
\beta_3&=\frac{\Gamma_{P1}\Gamma_P\Gamma_{J'J_1''}({}_1\Gamma_1\gamma\Gamma-4\Gamma\Omega_1\omega_1-4{}_1\Gamma\Omega\omega_1-4{}_1\gamma\Omega_1\Omega)}{({}_1\Gamma^2+4\Omega_1^2)(\Gamma^2+4\Omega^2)({}_1\gamma^2+4\omega_1^2)}.
\end{aligned}\right\} \tag{7}$$

Here ω_1, Ω_1, and Ω are the Larmor frequencies for J_1'', J_1', and J'. The form of the Hanle signal is given in Fig. 3 for $\Omega=\Omega_1$, $\Gamma={}_1\Gamma$, $\omega_1/{}_1\gamma\gg\Omega_1/{}_1\Gamma$. Curves *1* and *4* demonstrate the signal of the lower level J_1'' for a scale $\omega_1/{}_1\gamma\sim 1$, where the magnetism of the upper state is unimportant and the width of the contour is determined only by the ratio $g_1''/{}_1\gamma$ and correspond to the expressions

$$P^Q(\mathbf{E}_{P1}\|\mathbf{E}_P)=\frac{2+4(\omega_1/{}_1\gamma)^2}{3+8(\omega_1/{}_1\gamma)^2}, \tag{8}$$

$$P^Q(\mathbf{E}_{P1}\perp\mathbf{E}_P)=\frac{-4(\omega_1/{}_1\gamma)^2}{1+8(\omega_1/{}_1\gamma)^2}. \tag{9}$$

Curves *2* and *5* in Fig. 3 refer to a scale of $\Omega_1/{}_1\Gamma\sim 1$, in which the Hanle effect of the excited level J_1' appears (the effect of the ground state is already completely developed and does not appear in this scale) and has a Lorentzian shape

$$P^Q=\frac{\pm 0.5}{1+4(\Omega_1/{}_1\Gamma)^2}, \tag{10}$$

where the $+$ or $-$ refer to $\mathbf{E}_{P1}\|\mathbf{E}_P$ (curve *2*) or $\mathbf{E}_{P1}\perp\mathbf{E}_P$ (curve *5*).

Curves *3* $(\mathbf{E}_{P1}\|\mathbf{E}_P)$ and *6* $(\mathbf{E}_{P1}\perp\mathbf{E}_P)$ in Fig. 3 demonstrate the superposed Hanle signals of the levels J_1' and J_1'' for which $\omega_1/{}_1\gamma=15\Omega_1/{}_1\Gamma$. Such a relation is real, for example, for *B–X* transitions of alkali dimers Na_2 and K_2.[3] It is evident that at first the narrower Hanle effect of the state J_1'' appears and then J_1'. For studying the Hanle effect of the level J_1'' the geometry of the experiment with $\mathbf{E}_{P1}\perp\mathbf{E}_P$ is best, because the maximum signal amplitude is greater (1/2 instead of 1/6); and, in addition, the signals of the ground and excited states have different signs and therefore are separated from one another better. It is interesting to note that the minimum value of P^Q, determined by curve *6*, is less than the limit $P^Q=-0{,}5$ for curves *4* and *5* in Fig. 3.

P,R transition, LP *excitation*. In this case the coefficients F_Q^K in Eqs. (3) and (4) equal, $F_0^0=\Gamma_P\varphi_0^0/3$, $F_0^2=\Gamma_P\varphi_0^0/30$, $F_{\pm 2}^2=\Gamma_P\varphi_0^0\sqrt{2}/20\sqrt{3}$, and the expression analogous to Eq. (6) has the form

$$P^{P,R}=(\beta_3\pm\beta_2)/(9\tau_1\pm\beta_1). \tag{11}$$

Here again we consider the case $\omega_1/{}_1\gamma\gg\Omega_1/\Gamma$ (Fig. 3). For the ratio $\omega_1/{}_1\gamma\sim 1$ (curves *1* and *4*) we obtain

$$P^{P,R}(\mathbf{E}_{P1}\|\mathbf{E}_P)=\frac{1+2(\omega_1/{}_1\gamma)^2}{5+18(\omega_1/{}_1\gamma)^2}, \tag{12}$$

$$P^{P,R}(\mathbf{E}_{P1}\perp\mathbf{E}_P)=\frac{-(\omega_1/{}_1\gamma)^2}{2+9(\omega_1/{}_1\gamma)^2}. \tag{13}$$

The expressions differ from Eqs. (8) and (9) by the smaller signal amplitude. For the ratio $\Omega_1/{}_1\Gamma\sim 1$ the effect of the excited state (curves *2* and *5*) appears

$$P^{P,R}=\frac{\pm 1/9}{1+4(\Omega_1/{}_1\Gamma)^2} \tag{14}$$

with amplitude 1/9, which is less than the value 1/7 for J', $J''\gg 1$ for the isotropic lower level.[16] At the same time, for the Q transition the amplitude of the effect [Eq. (10)] coincides with 1/2 for the isotropic lower state, which is easy to understand from the classical description.[16,17] The superposed signal for $\omega_1/{}_1\gamma=50\Omega_1/3_1\Gamma$ is shown in Fig. 3 (curves *3* and *6*).

P,R transitions, CP *excitation*. We consider the case of CP excitation in both cycles and with observation directed along the X axis (Fig. 1); $\mathbf{B}\|OZ$. We choose at first the case of right-handed polarized (r transition) R type in the cycles $J''\to J'$, $J_1''\to J_1'$ and denote them by $(R\uparrow,r)$ and $(R\uparrow,r)_1$, respectively. Then, according to Eq. (3) $F_0^0=\Gamma_P\varphi_0^0/3$, $F_{\pm 1}^1=\pm\Gamma_P\varphi_0^0/6\sqrt{2}$, $F_0^2=-\Gamma_P\varphi_0^0/60$, $F_{\pm 2}^2=\Gamma_P\varphi_0^0\sqrt{6}/120$. The expression for the degree of circularity $C=(I_r-I_l)/(I_r+I_l)$, where $I_{r,l}$ are the components of the intensity polarized either right-handed or left-handed, in the assumption of an *R*-type transition $J_1'\to J_2''$, $\Gamma_K={}_1\Gamma_K=\Gamma$, $\Omega_1=\Omega$, ${}_1\gamma_x={}_1\gamma$, has the form

$$C=\frac{98(\mu_1+\mu_2)+14(\mu_3+\mu_4)}{128\nu_1+98\mu_2+5(\mu_5+\mu_7+\mu_8)+14\mu_6}. \tag{15}$$

For each substitution $R\leftrightarrow P$ or $r\leftrightarrow l$ in any of the three cycles the signs in Eq. (15) in front of μ_i with even i are reversed. The designations in Eq. (15) are the following:

$$\begin{aligned}
\nu_1&=\frac{1}{{}_1\gamma\Gamma^2}, \quad \mu_1=\frac{{}_1\gamma\Gamma^2-2\Gamma\Omega\omega_1-{}_1\gamma\Omega^2}{(\Gamma^2+\Omega^2)^2({}_1\gamma^2+\omega_1^2)},\\
\mu_2&=\frac{1}{{}_1\gamma(\Gamma^2+\Omega^2)}, \quad \mu_3=\frac{{}_1\gamma\Gamma^2+{}_1\gamma\Omega^2}{(\Gamma^2+\Omega^2)^2({}_1\gamma^2+\omega_1^2)},\\
\mu_4&=\frac{{}_1\gamma\Gamma^2-6\Gamma\Omega\omega_1-2{}_1\gamma\Omega^2}{(\Gamma^2+\Omega^2)(\Gamma^2+4\Omega^2)({}_1\gamma^2+4\omega_1^2)},\\
\mu_5&=\frac{{}_1\gamma\Gamma^2-8\Gamma\Omega\omega_1-4{}_1\gamma\Omega^2}{(\Gamma^2+4\Omega^2)^2({}_1\gamma^2+4\omega_1^2)},\\
\mu_6&=\frac{{}_1\gamma\Gamma^2-3\Gamma\Omega\omega_1-2{}_1\gamma\Omega^2}{(\Gamma^2+4\Omega^2)(\Gamma^2+\Omega^2)({}_1\gamma^2+\omega_1^2)},\\
\mu_7&=\frac{1}{{}_1\gamma(\Gamma^2+4\Omega^2)},\\
\mu_8&=\frac{{}_1\gamma\Gamma-\Omega\omega_1}{\Gamma(\Gamma^2+\Omega^2)({}_1\gamma^2+\omega_1^2)},\\
\mu_9&=\frac{{}_1\gamma\Gamma-\Omega\omega_1}{\Gamma(\Gamma^2+4\Omega^2)({}_1\gamma^2+4\omega_1^2)}.
\end{aligned} \tag{16}$$

Equation (15) simplifies for $\omega_1/{}_1\gamma\gg\Omega/\Gamma$, where for $\omega_1/{}_1\gamma\sim 1$ the magnetism of the upper levels does not appear

$$C=\frac{28+119\omega_1^2/{}_1\gamma^2+49\omega_1^4/{}_1\gamma^4}{32+141\omega_1^2/{}_1\gamma^2+67\omega_1^4/{}_1\gamma^4}. \tag{17}$$

If in the transitions $J''\to J'$, $J_1''\to J_1'$ one makes an odd number of substitutions $R\leftrightarrow P$ or $r\leftrightarrow l$, the expression has the form

$$C=\frac{-7(1+7\omega_1^2/{}_1\gamma^2)(\omega_1/{}_1\gamma)^2}{4+29\omega_1^2/{}_1\gamma^2+67\omega_1^4/{}_1\gamma^4}. \tag{18}$$

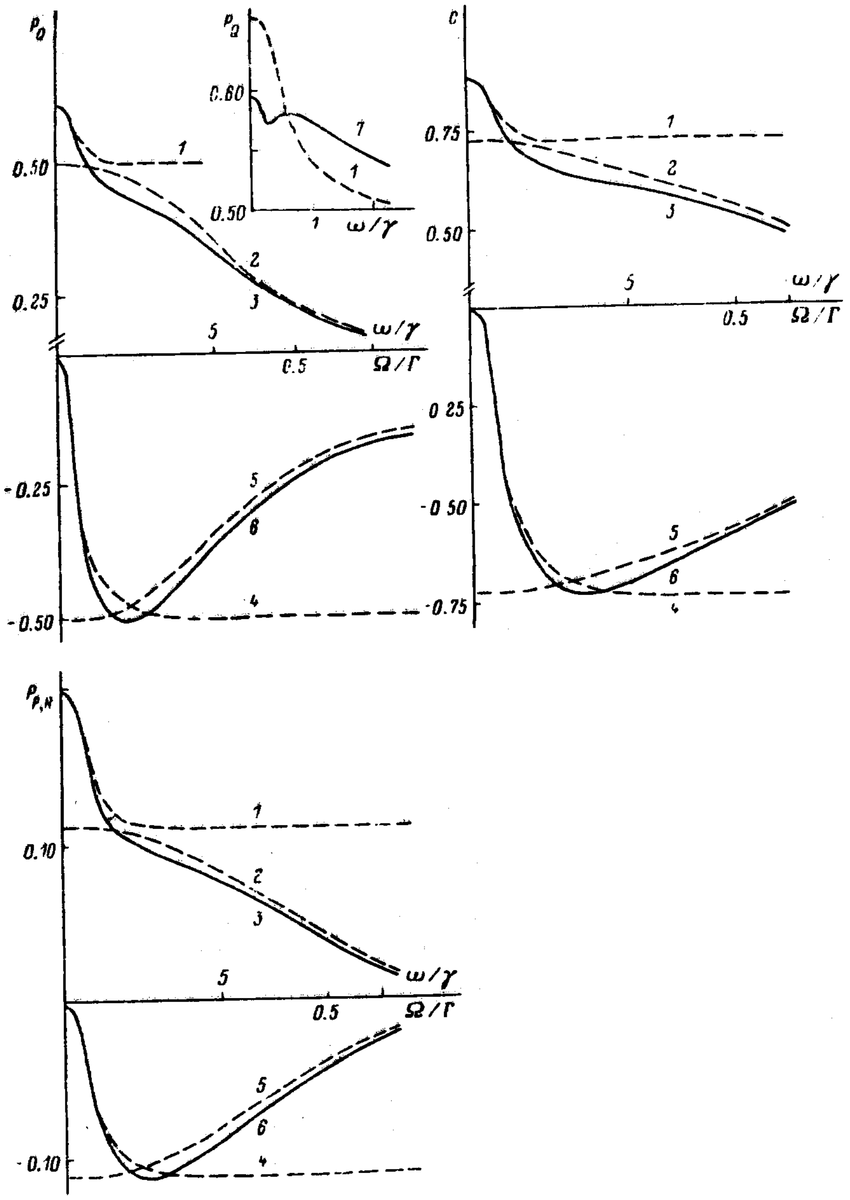

FIG. 3. The level-crossing signals.

The form of the signals of Eqs. (17) and (18) are shown in Fig. 3 (curves *1* and *4*); in the case of Eq. (18) the amplitude of the signal from level J''_1 is ~ 0.75, i.e., very large. Curves *2* and *5* describe the signal from the level J'_1 for the ratio $\Omega/\Gamma \sim 1$, and curves *3* and *6* for $\omega_1/{}_1\gamma = 50\Omega/3\Gamma$. The value of C for curves *2* and *5* for $\omega_1 = 0$ equals $\pm 5/7$ in agreement with the known result for $J'', J' \gg 1$.[16]

The cases considered (for Q transitions with $J'', J' \gg 1$ the orientation does not arise) describe the anticipated form of the crossing signals for all the basic variations of polarization states and types of transitions.

THE KINETICS OF THE TRANSITION PROCESS

One can obtain direct information about rates of the reaction ${}_1\gamma_\varkappa$ for PM ${}_1\varphi^\varkappa_q$ by the known dynamical method.[18,19] Pumping $J'' \to J'$ with pulses of duration $\Delta t \ll {}_1\gamma_\varkappa^{-1}$ in the presence of an external magnetic field enables one to observe the effects of quantum beats (QB) between the magnetic sublevels M''_1 of the state J''_1. In the background of the decay of the intensity I_i for $t > 0$ (Fig. 1) oscillations appear with frequency $q\omega_1$ or QB (we assume $\Gamma_{sp} \gg {}_1\gamma_\varkappa$). We describe the QB in a magnetic field $\mathbf{B} \| OZ$ for pulsed pumping (by populating) when $\Gamma_P = G\delta(t)$. For LP excitation $\mathbf{E}_P \| \mathbf{E}_{P1} \| OY$ for $\Gamma = 0$ one obtains from Eqs. (1)–(5)

$$\left.\begin{aligned} I_1^Q(\mathbf{E}_{P1} \| \mathbf{E}_P) &= 6G\left(7e^{-{}_1\gamma_0 t} + 2e^{-{}_1\gamma_2 t} + 6e^{-{}_1\gamma_2 t}\cos 2\omega_1 t\right), \\ I_3^Q(\mathbf{E}_{P1} \| \mathbf{E}_P) &= 2G\left(7e^{-{}_1\gamma_0 t} + 2e^{-{}_1\gamma_2 t}\right), \\ I_1^{P,R}(\mathbf{E}_{P1} \| \mathbf{E}_P) &= 2G\left(14e^{-{}_1\gamma_0 t} + e^{-{}_1\gamma_2 t} + 3e^{-{}_1\gamma_2 t}\cos 2\omega_1 t\right), \\ I_2^{P,R}(\mathbf{E}_{P1} \| \mathbf{E}_P) &= 3G\left(7e^{-{}_1\gamma_0 t} + e^{-{}_1\gamma_2 t}\right). \end{aligned}\right\} \tag{19}$$

For $\mathbf{E}_P \perp \mathbf{E}_{P1} \| OX$ we have $I_1(\mathbf{E}_{P1} \perp \mathbf{E}_P) = I_2(\mathbf{E}_{P1} \| \mathbf{E}_P)$, and $I_2(\mathbf{E}_{P1} \perp \mathbf{E}_P)$ differs from $I_1(\mathbf{E}_{P1} \| \mathbf{E}_P)$ by a minus sign in the term with $\cos 2\omega_1 t$.

For CP pumping in the same notation as that of Eqs. (15)–(18)

$$I(P\downarrow, l)_2 = I(R\downarrow, r)_2 = \tag{20}$$

$$G\left(42e^{-{}_1\gamma_0 t} + 42e^{-{}_1\gamma_1 t}\cos\omega_1 t + 1.5e^{-{}_1\gamma_2 t} + 4.5e^{-{}_1\gamma_2 t}\cos 2\omega_1 t\right),$$

$$I(P\downarrow, r)_2 = I(R\downarrow, l)_2 = G\left(7e^{-{}_1\gamma_0 t} - 0.25e^{-{}_1\gamma_2 t} - 0.75e^{-{}_1\gamma_2 t}\cos 2\omega_1 t\right). \quad (21)$$

For an odd number of substitutions $R\leftrightarrow P$ or $r\leftrightarrow l$ in the cycles of excitation for $I(P\downarrow,l)_2 = I(R\downarrow,r)_2$ Eq. (21) is applicable, but for $I(P\downarrow,r)_2 = I(R\downarrow,l)_2$ Eq. (20) is applicable, where the sign before the term with $e^{-{}_1\gamma_1 t}$ is changed. An even number of such substitutions preserves Eqs. (20) and (21). It is evident that in Eq. (21), unlike Eq. (20), the decay of the orientation ${}_1\varphi_q^1$ does not appear.

ESTIMATE OF THE CONCENTRATION FOR PUMPING

Until now it has been assumed that in both cycles (Fig. 1) the PM of the lower level does not change, i.e., $\Gamma_P/\gamma_\varkappa \ll 1$, $\Gamma_{P1}/{}_1\gamma_\varkappa \ll 1$ (linear response). Let us consider a more complex case where $\Gamma_P/\gamma_\varkappa \gtrsim 1$ in the cycle $J'' \to J'$ and in the level J'' the light field produces PM $\varphi_q^\varkappa$ of different rank and couples with the PM f_Q^K of the level J'. Such an emptying of the ground state of diatomic molecules was studied in Refs. 1–5, 15, 17, 18, and 20. Instead of by Eq. (1) the system is described by a system of coupled kinetic equations, which take into account the effect of the strong light field. The system was solved by us numerically with the use of an algorithm for $J', J'' \to \infty$,[15] and with the assumption $\gamma_\varkappa$ and g are identical for J' and J''. The PM $\varphi_q^\varkappa$ (to $\varkappa = 10$) and f_Q^K (to $K = 2$) were determined for the steady-state solution for specific Γ_P/γ, from which by Eqs. (2)–(5) ${}_1\varphi_q^\varkappa, f_Q^K$ were found assuming the light field was weak in the cycle $J_1'' \to J_1'$.

An example of the computer calculation of the Hanle signal is given in Fig. 3 (curve *7*) for the Q transition for LP excitation. The PM $\varphi_q^\varkappa$ of even rank produced in the level J'', are transferred by light to J', and after spontaneous decay to J_1'' affect the signal in the cycle $J_1'' \to J_1' \to J_2''$. This broadens the signal, decreases its amplitude, and gives rise to the appearance of nonmonotonic structure connected with the complex effect of the PM of both levels $\varphi_q^\varkappa$ and ${}_1\varphi_q^\varkappa$ of rank $\varkappa = 4$ and $\varkappa = 6$.[20] The PM $\varphi_q^\varkappa$ and ${}_1\varphi_q^\varkappa$ have different signs and the ${}_1\varphi_q^\varkappa(B)$, unlike the $\varphi_q^\varkappa(B)$, are not broadened by the light field, because $\Gamma_{P1} \ll \gamma$.

We estimate which part of the equilibrium population $\overline{\varphi_0^0}$ of the starting level J'' one can pump into the level J_1''. For $\Gamma_P/\gamma \ll 1$, $\Gamma_{P1}/{}_1\gamma \ll 1$ there follows from Eqs. (2)–(4)

$${}_1\varphi_0^0 = \frac{\Gamma_P \Gamma_{J'J_1''} \overline{\varphi_0^0}}{3\Gamma_1 \gamma} \quad (22)$$

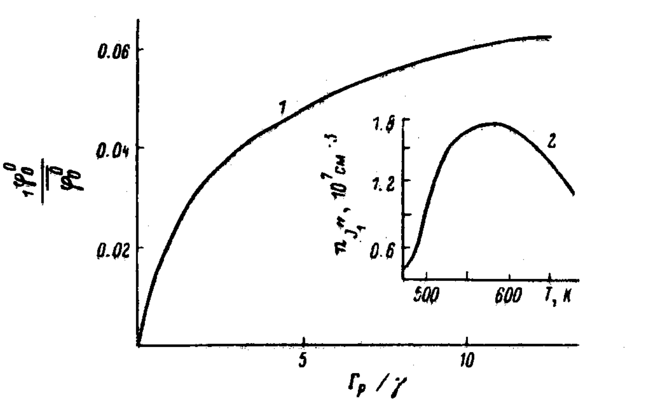

FIG. 4. Population of level ${}_1\varphi_0^0 J_1''$ with respect to the equilibrium population of the level $\varphi_0^0 J''$ vs the parameter Γ_P/γ (*1*) and computation of the concentration $n_{J_1''}(T) = {}_1\varphi_0^0$ for $^{39}K_2(X^1\Sigma_g^+)$ (*2*).

The discussed computations enable one to establish to which measure the emptying of level J'' is by the mixing process for pumping into J_1'' [Fig. 4 curve *1*). It is evident that increasing Γ_P is effective only up to a definite limit, after which (for $\Gamma_P/\gamma \gtrsim 10$) ${}_1\varphi_0^0/\overline{\varphi_0^0}$ increases only insignificantly.

For increasing ${}_1\varphi_0^0$ the largest total concentration of molecules $[A_2]$ is advantageous. For example, however, in vapors of alkali metals the concentration of dimers $[A_2]$ grows with increasing temperature[21]; but the relaxation rates γ, and Γ increase, because of collisions with atoms A (the predominant component in the vapor), because

$$\gamma = \gamma_0 + \sigma N_A \bar{v}_r, \quad \Gamma = \Gamma_{sp} + Q N_A \bar{v}_r, \quad (23)$$

where σ and Q are effective cross sections, N_A is the concentration of atoms, γ_0 is connected with the noncollisional relaxation because of the thermal motion (pass through) of the molecules through the beam.[1] We estimate ${}_1\varphi_0^0$ in the example of well-radiated dimers of potassium in potassium vapor. The quantity φ_0^0 was computed for $v'' = 1$, $J'' = 73$ for the total concentration of $[K_2]$ from Ref. 21 with consideration of the distribution over VR levels for a given temperature, and with γ and Γ from Eq. (23). We took $\gamma_0 = 4\times10^5$ sec^{-1} $\Gamma_P = 10^6$ sec^{-1}, $\sigma(K_2+K) = 3.3\times10^{-4}$ cm^2,[18] $\Gamma = 86.3\times10^6$ sec^{-1},[3] $Q(K_2+K) = 6.4\times10^{-14}$ cm^2.[22] The values of $\Gamma_{J'J_1''}$ were determined in Ref. 23; and one might choose completely the transition with $\Gamma_{J'J''} \approx 0.05\Gamma_{sp}$. Substitution of these quantities into Eq. (22) leads to the dependence of ${}_1\varphi_0^0$ shown in Fig. 4 (curve *2*), which for $T \approx 570$ K has a maximum ${}_1\varphi_0^0 \approx 1.7\times10^7$ cm^{-3}. If one goes the way of increasing Γ_P, using a laser with high spectral power, then ${}_1\varphi_0^0$ increases, but with this it is necessary to take into account saturation, because of emptying [Fig. 4 (curve *1*)].

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