

Hanle effect in the ground electronic state of dimers with allowance for the finite value of angular momentum

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The device of polarization moments is used to analyze the expected signals of the Hanle effect of the vibrational-rotational (VR) level of the ground electronic state of dimers during its laser emptying. All the types of molecular transitions allowed for dimers are considered. It is shown that the shape of the Hanle signal for states with a small angular momentum differs qualitatively from the signal shape for states with a high value of angular momentum. Moreover, as J'' decreases, the shape of the Hanle signal becomes more complex; this makes it possible to hope for the study of such VR characteristics of the level as the rate of relaxation of high-rank polarization moments. It was found that the types of transitions $Q \uparrow Q \downarrow$, $P \uparrow P \downarrow$ and $P \uparrow R \downarrow$ are the most convenient for studying the magnetic and relaxation characteristics of VR levels of the ground state of dimers at low values of J'' .

Along with the study of atoms, the Hanle effect (strong depolarization of scattered light by an external magnetic field¹) is used quite extensively also in the study of vibrational-rotational (VR) levels v', J' of electronically excited states of dimers. The method makes it possible to study various characteristics of a state, such as the g factor and radiative lifetime,²⁻⁴ or the rate and cross section of collisional relaxation.^{5,6}

When the rate of absorption of laser light Γ_p becomes comparable to the relaxation rate γ_x of the lower level of a transition, i.e., to the rate of VR relaxation of the v'', J'' level of the ground electronic state of dimers, optical pumping by emptying is produced. The VR level of the ground electronic state becomes optically pumped.⁷ Moreover, in contrast to atoms, an open process takes place in molecules⁸ when the molecule which has absorbed light has a low probability of returning to the original VR level as a result of the next radiative decay. Such a situation is due to the large number of allowed VR transitions in the spectrum of laser-induced fluorescence (LIF) of the molecule.⁹ When optical pumping of molecules takes place in an external magnetic field, there is manifested the Hanle effect of both the excited VR level and the VR level of the ground electronic state of the molecule.¹⁰ For a number of molecular states, the Hanle signal from the excited level turns out to be considerably broader than the signal from the ground level.¹¹ Such a situation makes it possible, in experimentally obtained Hanle profiles, to separate the contribution of the ground and excited VR levels and as a result, to determine the magnetic moments and rates of relaxation in the ground electronic state of the molecule (see, for example, Refs. 10 and 12).

Thus, far the analysis of the shape of a nonlinear Hanle signal has been made in the asymptotic limit of high angular momenta.^{13,14} This model has also been used for treating experimental results (see, for example, Ref. 15). This approach is justified to some degree by the fact that in many cases, the VR levels of dimers coupled by an optical transition have values of rotational quantum number $J > 10$.¹¹ At the same time, the convergence of the degree of polarization to the classical limit of high angular momenta as the quantum number J increases in the case of optical pumping of molecules is strongly dependent on the type of optical transitions. Thus, for transitions of types $Q \uparrow Q \downarrow$ ($J'' \rightarrow J' = J'' \rightarrow J''$

$= J''$), $R \uparrow P \downarrow$ ($J'' \rightarrow J' = J'' + 1 \rightarrow J'' + 2$) and $P \uparrow R \downarrow$ ($J'' \rightarrow J' = J'' - 1 \rightarrow J'' = J'' - 2$), in the absence of an external magnetic field, the limit of high angular momenta is reached as early as $J'' \sim 10$. However, for transitions of types $P \downarrow P \downarrow$ ($J'' \rightarrow J' = J'' - 1 \rightarrow J'' = J''$) and $R \downarrow R \downarrow$ ($J'' \rightarrow J' = J'' + 1 \rightarrow J'' = J''$), the asymptotic limit is not reached until $J'' \sim 100$.⁷⁻¹⁶

It is necessary, therefore, to perform an analysis of expected signals of the Hanle effect of the ground state of dimers for VR levels with a low value of angular momentum. For different types of molecular transitions, such signals can be calculated by means of polarization moments (PM).¹⁷ The equations of motion of PM for states with an arbitrary value of angular momentum are given in Ref. 18. We will write them in the compact form¹⁹

$$\begin{aligned} \Gamma_p \sum_{Xx} \kappa_{F^{Xx}} \{ \Phi^{(X)} \otimes \varphi^{(x)} \}_Q^K - \Gamma_p \left(\frac{\Pi_{J''}}{\Pi_{J'}} \right)^2 \\ \times \sum_{XK'} \kappa_{A^{XK'}} \{ \Phi^{(X)} \otimes f^{(K')} \}_Q^K - (\Gamma_K - lQ\Omega) f_Q^K = 0, \quad (1a) \\ -\Gamma_p \sum_{Xx'} \kappa_{A^{Xx'}} \{ \Phi^{(X)} \otimes \varphi^{(x')} \}_Q^K \\ + \Gamma_p \left(\frac{\Pi_{J'}}{\Pi_{J''}} \right)^2 \sum_{XK} \kappa_{F^{XK}} \{ \Phi^{(X)} \otimes f^{(K)} \}_Q^K - (\gamma_x - lq\omega) \varphi_Q^K \\ + \Gamma_{J',J''} c_x \delta_{Kx} \delta_{Qq} f_Q^K + \lambda_q^2 \delta_{x0} \delta_{q0} = 0, \quad (1b) \end{aligned}$$

where

$$\kappa_{A^{Xx'}} = \frac{[1 + (-1)^{x+X+x'}]}{2} \frac{\Pi_{J',Kx'}}{\Pi_x} (-1)^{J''-J'+x'} \begin{Bmatrix} x & X & x' \\ J'' & J'' & J'' \end{Bmatrix} \begin{Bmatrix} 1 & 1 & X \\ J'' & J'' & J'' \end{Bmatrix}, \quad (2)$$

$$\kappa_{F^{Xx}} = \frac{\Pi_{J',Kx}}{\Pi_{J''K}} (-1)^{x+1} \begin{Bmatrix} K & J' & J' \\ X & 1 & 1 \\ x & J'' & J'' \end{Bmatrix}, \quad (3)$$

$$c_x = (-1)^{J''-J'+x+1} \Pi_{J''J'} \begin{Bmatrix} J'' & J'' & x \\ J'' & J'' & 1 \end{Bmatrix}. \quad (4)$$

Here φ_Q^K and f_Q^K are the PM for the ground and excited levels, $\omega = g''\mu_B H/\hbar$ and $\Omega = g'\mu_B H/\hbar$ are the frequencies of Zeeman splitting of the J'' and J' states under action of the

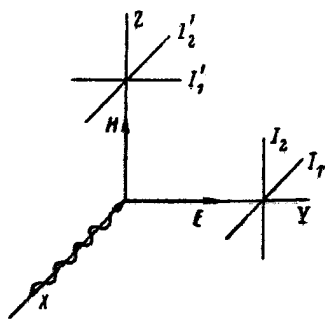


FIG. 1. Geometry of transverse and longitudinal recordings of the Hanle signal.

external magnetic field H (g'' , g' are the corresponding Landé factors, and μ_B is the Bohr magneton), $\Pi_{ab} = \sqrt{(2a+1)(2b+1)}$, and the expressions in braces are the $6j$ and $9j$ symbols. The constant $\gamma_q^\alpha \delta_{x0} \delta_{q0}$ is the rate of isotropic relaxation of the population of the rotational level J'' , Γ_K is the rate of decay of the PM, and $f_{J''}^K$ is the rate of reverse spontaneous transitions. The coefficients ${}^K A_{J''}^{XK'}$ and ${}^X F_{J''}^{XK}$ differ from ${}^X A_{J''}^{XK}$ and ${}^K F_{J''}^{XK}$ in that the first pair represents stimulated emission of light, and the second pair represents absorption. To obtain the numerical value of ${}^K A_{J''}^{XK}$ and ${}^X F_{J''}^{XK}$, it is necessary to use Eqs. (2) and (3), respectively, in which J' and J'' change places. The tensor $\Phi^{(X)}(e)$ describes the polarization of light,¹⁷ and $\{\Phi^{(X)} \otimes \varphi^{(X)}\}_Q^K$ denotes an irreducible tensor product.

The intensity of LIF with polarization e' on the $(v', J') \rightarrow (v'', J'')$ transition is determined by the PM $f_{J''}^{K'}$ and can be obtained in accordance with the equation¹⁷

$$I(e') = I_0 (-1)^{J'+J''} \sum_K \Pi_K \left\{ \begin{matrix} 1 & 1 & K \\ J' & J' & J'' \end{matrix} \right\} \sum_Q (-1)^Q f_Q^K \Phi_Q^K(e'). \quad (5)$$

In general, the system (1a), (1b) contains $(2J''+1)^2 + (2J'+1)^2$ coupled equations. A successful solution by computer makes it necessary to use the symmetry properties of these equations, which are analyzed in Refs. 14, 16, and 20.

We will begin the analysis of the dependence of the degree of polarization $\mathcal{P} = (I'_1 - I'_2)/(I'_1 + I'_2)$ on the external magnetic field in the presence of the nonlinear Hanle effect with the traditional geometry of observation along the magnetic field (Fig. 1). Figure 2 shows the dependence on the magnitude of the dimensionless parameter ω/γ for different values of the angular-momentum quantum number J'' . All possible types of molecular transitions are considered. In the computer calculation, the following numerical values of the molecular constants were assumed: $\gamma_x = \gamma = 0.3 \mu\text{sec}^{-1}$, $\Gamma_p = 10.0 \mu\text{sec}^{-1}$, $\Gamma_{J''} = 0$, $\Gamma_K = \Gamma \gg \gamma$, Γ_p . We considered the case in which the Hanle profile of the low level was substantially narrower than that of the excited level, i.e., $\omega/\gamma \gg \Omega/\Gamma$. The accepted relationships of the molecular constants were close to the actual ones for a whole series of homonuclear diatomic molecules.¹¹ For comparison, Fig. 2 also shows a curve corresponding to a state with a very large value of angular momentum, obtained in the asymptotic approximation $J'' \rightarrow \infty$.¹⁴ In this case, only the PM of rank $\kappa \leq 10$, $K \leq 2$ was taken into account in the calculation. With the accepted values of the molecular constants, this ensures that the values of \mathcal{P} are obtained with a

relative error of the numerical calculation ≤ 0.0001 . There is no point in this case in taking into account a large quantity of PM of the excited state J' , since the equations for φ_q^X and f_Q^K at the values of the molecular constants employed are separated and can be solved successively.

In the curves obtained, for the nonlinear Hanle signal, there appears a series of characteristics which are qualitatively new in comparison with the previously studied limit $J'' \rightarrow \infty$.^{13,21,22} In particular, for transitions of the $Q \uparrow Q \downarrow$ type, the Hanle effect of the ground state for the level with $J'' = 1$ has the opposite sign in comparison with states with a different value of J'' , i.e., it results, not in repolarization, but in depolarization of LIF (Fig. 2). Further, for transitions of the $P \uparrow P \downarrow$ and $P \uparrow R \downarrow$ types for states with a small angular momentum, in contrast to states with $J'' \rightarrow \infty$, a narrow structure of the signal is clearly manifested at low values of the parameter ω/γ . For $Q \uparrow Q \downarrow$ transitions in the limit $J'' \rightarrow \infty$, such a structure was previously interpreted as the manifestation of a PM of rank $\kappa \geq 4$.^{22,23} It may be postulated that in this situation the structure is also due to the same causes. Note that with the selected calculation parameters for the curve corresponding to the transition type $P \uparrow R \downarrow$ and to the value $J'' = 2$, the amplitude of the predicted structure is very substantial and reaches the value $\Delta \mathcal{P} > 0.09$. At the same time, for transitions of the $P \uparrow R \downarrow$ type, the additional structure has maximum amplitude for mean values of quan-

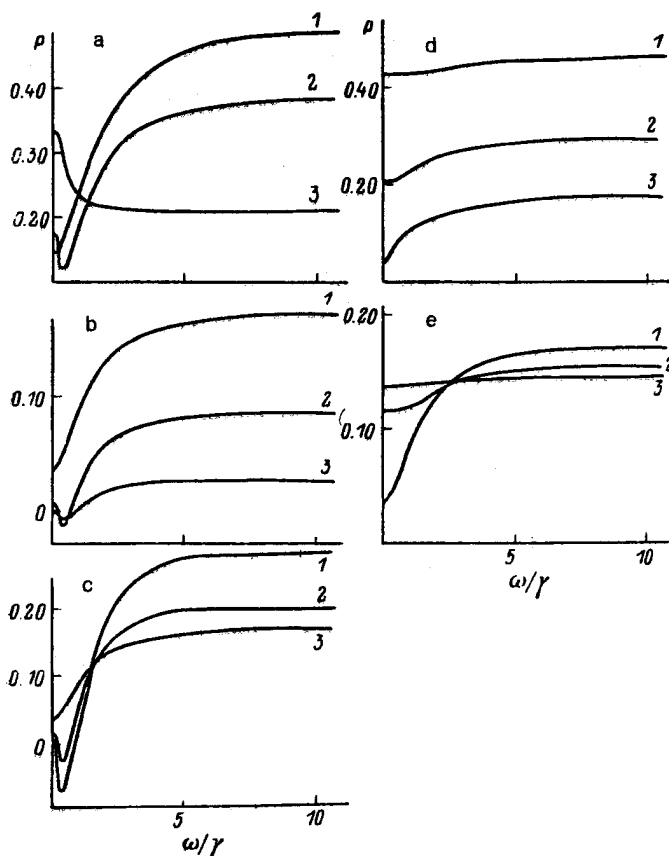


FIG. 2. Hanle effect of the ground state of dimers during observation along the magnetic field for the situation $\omega/\gamma \gg \Omega/\Gamma$, (a) $Q \uparrow Q \downarrow$, $J'' = 1 \rightarrow \infty, 2-3, 3-1$; (b) $P \uparrow P \downarrow$, $J'' = 1 \rightarrow \infty, 2-4, 3-2$; (c) $P \uparrow R \downarrow$, $J'' = 1-2, 2-1, 3 \rightarrow \infty$; (d) $R \uparrow R \downarrow$, $J'' = 1-1, 2-3, 3 \rightarrow \infty$; (e) $R \uparrow P \downarrow$, $J'' = 1 \rightarrow \infty, 2-3, 3-1$.

tum number J'' (Fig. 2). As a result of the appearance of structure in the Hanle signal for $P \uparrow P \downarrow$ and $P \uparrow R \downarrow$ transitions, the degree of polarization \mathcal{P} may even change sign, depending on ω/γ .

For $R \uparrow R \downarrow$ and $R \uparrow P \downarrow$ molecular transitions, the Hanle signal of the J'' level exhibits no additional structure and has a small amplitude (Fig. 2).

It was assumed in the calculations that PM of different ranks undergo relaxation at the same rates $\gamma_{\kappa} = \gamma$, $\Gamma_{\kappa} = \Gamma$. For states of dimers with high values of J' and J'' , this assumption has been confirmed experimentally.²⁴⁻²⁶ However, in the case of low values of J' and J'' , this situation can change. At the same time, since the structure of the nonlinear Hanle signal is sensitive to changes in the ratio γ_{κ}/γ_0 ,^{22,23} molecular transitions of the $P \uparrow R \downarrow$ type may turn out to be the most convenient for determining this ratio for levels with a low value of J'' .

The ratio $\omega/\gamma \gg \Omega/\Gamma$ used in the calculation of the curves in Fig. 2 may fail to hold in many cases. In particular, for absorption in the band of dimers $\Sigma \rightarrow \Pi$ with Hund's coupling type-a, the Landé factor of the J' level can be obtained as $g' = 1/[J'(J' + 1)]$.⁹ Then for states with small angular momenta, the reverse relationship may prove to apply, i.e., $\omega/\gamma \ll \Omega/\Gamma$. The latter inequality also holds when the excited state of the molecule is long-lived,²⁷ for example, the transitions in the X-B band of J_2 . In this case, because of the mag-

netic destruction of coherence in the excited state of the molecule during longitudinal observation, the degree of polarization of LIF falls to zero, and as a result, the Hanle effect of the ground state in this geometry cannot be observed. To record the Hanle signal in the ground state in the case $\omega/\gamma \ll \Omega/\Gamma$, one can study the degree of polarization of LIF $\mathcal{P} = (I_1 - I_2)/(I_1 + I_2)$ during observation across the external magnetic field (Fig. 1).²⁷ Figure 3 shows numerically modeled curves of expected signals of the nonlinear Hanle effect for different types of molecular transitions and different numerical values of angular momentum quantum number J'' . The following numerical values of the molecular constants were assumed in the calculation: $\gamma_{\kappa} = \gamma = 0.3 \mu\text{sec}^{-1}$, $\Gamma_{\kappa} = \Gamma = 100 \mu\text{sec}^{-1}$, $\Gamma_p = 10.0 \mu\text{sec}^{-1}$, $\Gamma_{J,J'} = 0.0$, $g' = 1.0$, $g'' = 10^{-5}$. To calculate the curves for $J'' \rightarrow \infty$, a method developed earlier^{14,20} was used, and only PM with $\kappa \leq 8$, $K \leq 6$ were included in the system of Eqs. (1a), (1b). This ensures an accuracy of calculation of \mathcal{P} of the order of 0.0003, which is completely satisfactory for comparing the expected signals. It follows from Fig. 3 that in transverse observation and with the selected values of molecular constants, the additional structure of the Hanle signal is not manifested for any type of transitions. The expected signal amplitude is large only for $Q \uparrow Q \downarrow$ and $P \uparrow R \downarrow$ transitions, and only for states with a small quantum number J'' . It is interesting to note that for the $P \uparrow P \downarrow$, $P \uparrow R \downarrow$, and $Q \uparrow Q \downarrow$ transitions, the shape of the Hanle curve for small values differs qualitatively from the shape of the curves for states with $J'' \rightarrow \infty$.

Analysis of the curves of Figs. 2 and 3 suggests that apart from the dependence on the relationships between ω/γ and Ω/Γ , the transition types $Q \uparrow Q \downarrow$, $P \uparrow P \downarrow$, and $P \uparrow R \downarrow$ are the most convenient for studying the VR levels of the ground state of the molecule at small values of J'' . In addition, the shape of the Hanle curves may differ qualitatively in the cases $J'' \sim 1$ and $J'' \rightarrow \infty$. In many cases, as J'' decreases, the Hanle curve becomes more complex and therefore more informative, which makes it possible to hope that such characteristics of the VR level as the relaxation rates of high-rank PM will be studied.

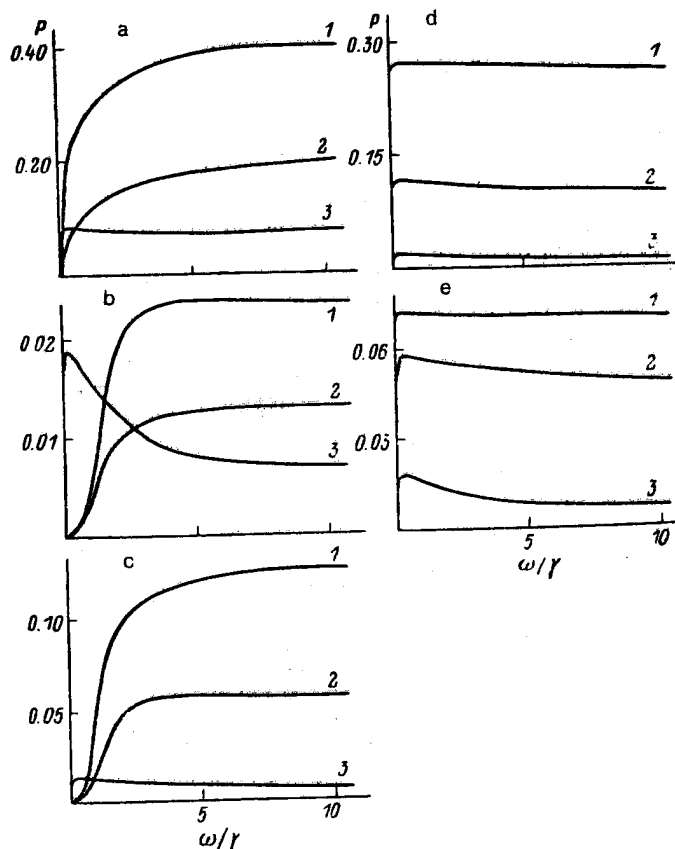


FIG. 3. Hanle effect of the ground state of dimers during observation across the magnetic field for the situation $\omega/\gamma \ll \Omega/\Gamma$, (a) $Q \uparrow Q \downarrow$, $J'' = 1 - 1, 2 - 3, 3 \rightarrow \infty$; (b) $P \uparrow P \downarrow$, $J'' = 1 - 1, 2 - 2, 3 \rightarrow \infty$; (c) $P \uparrow R \downarrow$, $J'' = 1 - 1, 2 - 2, 3 \rightarrow \infty$; (d) $R \uparrow R \downarrow$, $J'' = 1 - 1, 2 - 2, 3 \rightarrow \infty$; (e) $R \uparrow P \downarrow$, $J'' = 1 - 1, 2 - 2, 3 \rightarrow \infty$.

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