

# Zeeman quantum beats during the transient process after optical depopulation of the ground electronic state of diatomic molecules

M. P. Auzin'sh, M. Ya. Tamanis, and R. S. Ferber

*P. Stuchka Latvian State University, Riga*

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Theoretical and experimental investigations are made of quantum beats between the Zeeman sublevels  $M_J''$  of a vibrational-rotational level  $(v'', J'')$  of the ground electronic state  $\alpha''$  of diatomic molecules in an external magnetic field  $B$ . The beats occur in a transient process when a level optically depopulated by the  $(\alpha'', v'', J'') \rightarrow (\alpha', v', J')$  absorption transition relaxes to a thermal equilibrium state after the pump radiation is weakened to the intensity of a probe beam. Then, a harmonic component appears against the background of an exponential rise of the intensity caused by a probe fluorescence beam. An expansion in terms of the polarization moments is used in the asymptotic limit of large angular momenta to describe the expected signals in the case of short and long (compared with the characteristic nonradiative relaxation time) pump pulses. It is shown that in the case of linearly polarized excitation of the  $Q$  type and a specific experimental geometry one can expect either beats of frequency  $2\omega$  corresponding to alignment or with the frequency  $4\omega$  corresponding to relaxation of the hexadecapole moment; here,  $\omega = g_a \mu_0 B / \hbar$ , where  $g_a$  is the Landé factor of the  $(\alpha'', v'', J'')$  level. The experimentally determined dependence of the beat frequency on the magnetic field is used to find the value of the Landé factor for the  $(X^1\Sigma_g^+, 1, 72)$  level of the  $K_2$  molecule.

## INTRODUCTION

If a optical field excites coherently several levels, interference between them gives rise to quantum beats with a frequency equal to the level splitting during the decay of fluorescence after pulsed excitation (for a review see Ref. 1). A study of such "free" beats provides information on the nature of splitting of the excited levels without any restrictions imposed on the Doppler effect, and it has become an important method for investigating atomic systems using conventional and laser excitation sources.<sup>1,2</sup> In the case of excited states of gaseous molecules there are no fundamental differences and, beginning from Ref. 3, quantum beats are being used to study the hyperfine structure and to determine the Landé factors of electronically excited levels.

Our aim will be to extend the quantum beats method to the ground electronic state molecules. In contrast to an excited state, we now have to allow for the depopulation of the ground state during absorption. We shall consider a situation when the process of absorption depopulates a specific electronic-vibrational-rotational (EVR) level  $(\alpha'', v'', J'')$  of the ground electronic state  $\alpha''$  and the Zeeman sublevels of this state become coherent. This method makes it possible to study the magnetic properties of the state in question (usually diamagnetic), which is difficult to identify experimentally (particularly in the case of homonuclear molecules when radiative transitions between  $v'', J''$  inside the  $\alpha''$  state are forbidden) and to calculate theoretically.

The process of optical pumping of molecules by "depopulation" occurs when the rate of absorption  $\Gamma_p$  as a result of the  $(\alpha'', v'', J'') \rightarrow$  spherical transition (Fig. 1a) is comparable with the main competing process of collisional thermalization at a rate  $\gamma$  involving mixing between the  $(v'',$

$J'')$  levels it was first suggested in Ref. 4. The most direct method for investigating optical pumping and obtaining information on the relaxation rate  $\gamma$  is to record the kinetics of the transient process after the end of a depopulating pulse using either the absorption of a probe laser beam or the intensity of the fluorescence induced by this beam from the upper level spherical in the  $a \rightarrow b \rightarrow c$  cycle (Figs. 1a and 1b). The latter method is more sensitive (it was suggested in Refs. 5 and 6). In Ref. 5 and in the present study the probe beam is simply the pump beam attenuated at a moment  $t'_0$  to such a power density  $\rho_{pr}$  which cannot produce effects nonlinear in respect of the optical field (Fig. 1b). In this case an increase in the intensity of the laser-induced fluorescence at  $t' > t'_0$  (dashed curve in Fig. 1b) represents directly the recovery of the population of an optically depopulated lower level to the thermal equilibrium value, i.e., thermalization of this level. Under certain assumptions the signal of the transient process is exponential (for details see Ref. 7).

We shall report theoretical and experimental investigations of the transient process of thermalization of the lower state on application of an external static magnetic field causing splitting of the  $(\alpha'', v'', J'')$  level into its Zeeman components  $M_J''$ . It is shown that if the magnetic field  $B$  is orthogonal to the vector  $E$  of a linearly polarized exciting beam and to the direction of excitation (Fig. 1c), then the exponential function representing the transient process has superimposed periodic oscillations at frequencies corresponding to the splitting energy between the Zeeman sublevels with  $\Delta M_J'' = 2$  and 4 of the EVR level  $(\alpha'', v'', J'')$ . The proposed method makes it possible to determine spontaneously both the rate of relaxation  $\gamma$  and the magnetic constants, particularly the Landé factor of a single EVR level of the ground

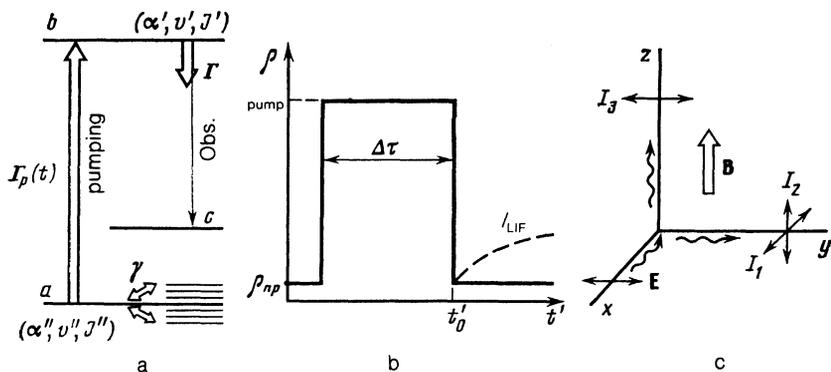


FIG. 1. a) Schematic representation of the optical pumping. b) Pump pulse with the dashed line representing the transient process of laser-induced fluorescence (LIF). c) Experimental geometry.

electronic state. It is important that although optical pumping (in the specific case of linearly polarized excitation causing optical alignment of the ground state) is essentially a nonlinear process, a signal is recorded in the linear absorption region at times  $t' > t'_0$  (Fig. 1b). This is an advantage compared with the method of a nonlinear resonance of beats as a result of harmonic modulated excitation<sup>8,9</sup> because the proposed method is free of nonlinear broadening effects and of a shift of the resonance signal. Naturally, in the ground state it is best to speak of "linear" beats in contrast in free quantum beats in an excited state, which appear when the excitation is stopped completely. The first observations of quantum beats in the transient process involving the ground state of dimers were obtained by us earlier.<sup>10,11</sup> The purpose of the present paper is to describe the process from a single standpoint using the technique of polarized moments for the cases of short ( $\Delta\tau \ll \gamma^{-1}$ ) and long ( $\Delta\tau \gg \gamma^{-1}$ ) pump pulses, and also to report the results of an experimental determination of the Landé factor of the ( $X^1\Sigma_g^+, v'', J''$ ) level of the  $K_2$  molecule.

### EXPRESSIONS FOR THE FLUORESCENCE INTENSITY

We shall assume that the linearly polarized pump radiation ceases to act at a time  $t' = t'_0$  (Fig. 1b) and that we are investigating the intensity of the laser-induced fluorescence  $b \rightarrow c$  with a given direction and a given polarization  $I_i$  ( $i = 1, 2, 3$ ), as shown in Fig. 1c; this fluorescence is excited by a weak probe beam at times  $t > t'_0$ . The expression for  $I_i$  in terms of the polarization moments of the excited state  $f_Q^K$  in the limit  $J', J'' \rightarrow \infty$  is of the form<sup>12,13</sup>

$$I_i \propto (-1)^\Delta \sum_K (2K+1)^{1/2} C_{1-\Delta 1 \Delta}^{K0} \sum_Q (-1)^Q f_Q^K \Phi_{-Q}^K(\mathbf{e}_i'), \quad (1)$$

where  $\Delta = J'_b - J''_c$ ;  $C_{cde}^{ab}$  is a Clebsch-Gordan coefficient;  $\Phi_{-Q}^K(\mathbf{e}_i')$  is a tensor introduced by D'yakov<sup>14</sup> for a specific polarization of the observation  $\mathbf{e}_i'$ . An analysis of the transient process at times  $t' > t'_0$  in terms of the polarization moments is made in Ref. 13 for the asymptotic limit  $J', J'' \rightarrow \infty$ . We shall therefore deal directly with the effects that appear on application of a magnetic field. The model of a process of optical alignment of the ground state postulating, in particular, that the rate of decay of  $\Gamma_K$  for the polarization moment

of the upper state  $f_Q^K$  or rank  $K$  is much greater than  $\gamma$  and the time dependence of  $f_Q^K$  depends on the time dependence of the polarization moment of the ground state  $\varphi_q^\kappa(t)$ , where  $t = t' - t'_0$ , i.e.,

$$f_Q^K(t) = \frac{\Gamma_p}{\Gamma_K - iQ\Omega} \sum_{\kappa, q} q^K D_q^\kappa \varphi_q^\kappa(t). \quad (2)$$

Here,  $\Gamma_p$  is the rate of optical excitation  $a \rightarrow b$ ;  $\Omega = g_b \mu_0 B / \hbar$  is the frequency of the magnetic splitting of the level  $b$ ;  $g_b$  is the Landé factor; the coefficient is given by<sup>12</sup>

$$q^K D_q^\kappa = (-1)^\Delta \left( \frac{2\kappa+1}{2K+1} \right)^{1/2} \times \sum_x (2X+1)^{1/2} C_{1\Delta 1-\Delta}^{X0} C_{X0 \kappa 0}^{X0} C_{XQ -q \kappa q}^{XQ} \Phi_{Q-q}^X(\mathbf{e}), \quad (3)$$

where  $\Delta = J'_b - J''_a$ ; the vector  $\mathbf{e}$  represents the polarization of the exciting light. During the transient stage characterized by  $t > 0$  and  $t \sim \gamma^{-1}$  the moments  $\varphi_q^\kappa$  created by the action of a strong optical field relax because of collisions at a rate  $\gamma_x$  and in a magnetic field with a frequency  $\omega = g_a \mu_0 B / \hbar$ , so that in the normalization of  $\varphi_0^0 = 1$  we obtain

$$\varphi_q^\kappa = \delta_{\kappa 0} - (\delta_{\kappa 0} - \varphi_q^\kappa) \exp[-(\gamma_x - iq\omega)t]. \quad (4)$$

Using Eqs. (1)–(4) we can express  $I_i(t)$  in terms of  $\varphi_q^\kappa$ . The expressions are not too cumbersome if we assume that  $\Gamma_K = \Gamma$  and  $\gamma_x = \gamma$  for all values of  $K$  and  $\kappa$  (the validity of this assumption is discussed in Refs. 7 and 13), and we shall also postulate that  $\Omega \ll \Gamma$ , i.e., we shall ignore the magnetic splitting of the upper state. Under these conditions we obtain the expressions for  $I_1$ ,  $I_2$ , and  $I_3$  where  $\Gamma_{pr}$  corresponding to  $\rho_{pr}$  (Fig. 1b):

$$I_1 = \frac{\Gamma_{pr}}{105\Gamma} [7 - e^{-\gamma t} (7 - 7_s \varphi_0^0 + 10_s \varphi_0^2 - 3_s \varphi_0^4) - 3\sqrt{70} e^{-\gamma t} \text{Re}(\varphi_4^1 e^{i\omega t})], \quad (5)$$

$$I_2 = \frac{\Gamma_{pr}}{105\Gamma} \{7 - e^{-\gamma t} (7 - 7_s \varphi_0^0 - 5_s \varphi_0^2 + 12_s \varphi_0^4) - \sqrt{2} e^{-\gamma t} [5\sqrt{3} \text{Re}(\varphi_2^2 e^{2i\omega t}) + 6\sqrt{5} \text{Re}(\varphi_2^4 e^{2i\omega t})]\},$$

$$I_3 = \frac{\Gamma_{pr}}{105\Gamma} \{ 21 - e^{-\gamma t} (21 - 21_s \varphi_0^0 + 30_s \varphi_0^2 - 9_s \varphi_0^4) - 6\sqrt{2} e^{-\gamma t} [5\sqrt{3} \operatorname{Re}({}_s \varphi_2^2 e^{2i\omega t}) - \sqrt{5} \operatorname{Re}({}_s \varphi_2^4 e^{2i\omega t})] + 3\sqrt{70} e^{-\gamma t} \operatorname{Re}({}_s \varphi_4^4 e^{4i\omega t}) \}. \quad (6)$$

Equations (5)–(7) are exact expressions which make it possible to study the standard geometry of linearly polarized excitation and observation in the case of  $Q$ -type transitions ( $J''_a = J'_b = J''_c$ ), for which the beat effect is strongest, and the simultaneous appearance in the laser-induced fluorescence of oscillations in a magnetic field  $\mathbf{B}$  and of decay of polarization moments of the ground state  ${}_s \varphi_q^\kappa$  created by a strong optical field. The expressions apply to any profile and length of an exciting light pulse; the only condition is the vanishing or weakening of a quantity which is linear in respect of the absorption of the optical field at the moment  $t = 0$ . Knowing  $I_1, I_2, I_3$ , we then have all these fluorescence signals usually observed under these conditions, including the signal proportional to the total intensity  $I_\Sigma = I_1 + I_2 + I_3$ , in which quantum beats also appear in contrast to the case of free beats in an excited state.<sup>1</sup> It is clear from Eq. (5) that the signal  $I_1$  manifests only beats of frequency  $4\omega$  related to relaxation of the hexadecapole moment  ${}_s \varphi_4^4$ . This, in principle, makes it possible to separate quantum beats associated purely with the polarization moments of rank four in the linear absorption region. In turn,  $I_2$  manifests only beats of frequency  $2\omega$ , but they are related to the relaxation of both  ${}_s \varphi_2^2$  and  ${}_s \varphi_4^4$  [see Eq. (6)], whereas  $I_3$  exhibits beats at the frequencies  $2\omega$  and  $4\omega$  [see Eq. (7)]. It should be noted that the moments of rank  $\kappa = 4$  vanish from the total intensity  $I_\Sigma$ , which is fully expected on the basis of an analysis in Ref. 13 which shows that in the linear absorption case these moments do not influence the total absorption. The expressions (5)–(7) make it possible to allow readily for the possibility of various relaxation rates  $\gamma_\kappa$  of the polarization moments of rank  $\kappa$ , which can be simply done by introducing into the factor  $\exp(-\gamma t)$  an index  $\kappa$  representing the rank of the next moment.

We must bear in mind that because of the generally complex nature of the polarization moments  ${}_s \varphi_2^2$  and  ${}_s \varphi_4^4$ , their oscillations in Eqs. (6) and (7) occurs at the same frequency  $2\omega$ , but have different phases because for  $\kappa = 2$  and 4, we have

$$\operatorname{Re}({}_s \varphi_2^2 e^{2i\omega t}) = [(\operatorname{Re} {}_s \varphi_2^2)^2 + (\operatorname{Im} {}_s \varphi_2^2)^2]^{1/2} \cos(2\omega t + \psi_\kappa), \quad (8)$$

where the phase is

$$\operatorname{tg} \psi_\kappa = \operatorname{Im} {}_s \varphi_2^2 / \operatorname{Re} {}_s \varphi_2^2. \quad (9)$$

We shall now consider the problem of finding the polarization moments of the ground state  ${}_s \varphi_q^\kappa$  which occur in Eqs. (5)–(7) and which are created by a strong optical field in two limiting cases: when the duration of action of pumping is  $\Delta\tau \ll \gamma^{-1}$  (excitation by a  $\delta$  pulse) and where the pumping is continued for some time, i.e.,  $\Delta\tau \gg (\gamma + \Gamma_p)^{-1}$ , and then is suddenly switched off (Fig. 1b).

## BEATS AFTER PUMPING WITH A $\delta$ -LIKE PULSE

The rate equations for the polarization moments of the ground state considered in the limit  $J', J'' \rightarrow \infty$  will be written down ignoring the reverse spontaneous and excited  $b \rightarrow a$  transitions, which gives<sup>13</sup>

$$d\varphi_q^\kappa/dt = -\Gamma_p \sum_{q', \kappa'} {}_q D_{q', \kappa'} {}_q \varphi_{q', \kappa'} - (\gamma_\kappa - iq\omega) \varphi_q^\kappa + \gamma_\kappa \varphi_q^\kappa \delta_{\kappa 0}. \quad (10)$$

In the case of an extremely short pulse acting at a moment  $t'_0$ , we shall assume that the rate of pumping is  $\Gamma_p = G\delta(t' - t'_0)$ . We shall solve Eq. (10) by expanding in powers of the parameter  $G < 1$ . The quantities  ${}_s \varphi_q^\kappa$  of interest to us in Eqs. (5)–(7) are the solution of Eq. (10) at the point  $t' = t'_0$ . In the first approximation the polarization moments  ${}_s \varphi_q^\kappa$  are found from the differential equation

$$d {}_s \varphi_q^\kappa/dt = -G\delta(t' - t'_0) {}_q D_0^{(\kappa)} \varphi_0^0 + {}_s \varphi_q^\kappa \gamma_\kappa \delta_{\kappa 0} - {}_s \varphi_q^\kappa \gamma_\kappa + iq\omega {}_s \varphi_q^\kappa \quad (11)$$

subject to the initial conditions  ${}_s \varphi_q^\kappa(t \rightarrow \infty) = {}_s \varphi_q^\kappa \delta_{\kappa 0}$ , where  ${}_s \varphi_0^0$  represents the population of the lower level not affected by the action of the optical field. The equations for finding the next approximations are derived and solved in the same way. To within terms containing  $G^3$ , the solution is of the form (with the equilibrium population  ${}_s \varphi_0^0$  normalized to unity)

$$\begin{aligned} {}_s \varphi_0^0 &= 1 - G/3 + G^2/5 - G^3/7, & {}_s \varphi_0^2 &= G/15 - 2G^2/35 + G^3/21, \\ {}_s \varphi_2^2 &= \sqrt{6} G/30 - \sqrt{6} G^2/35 + \sqrt{6} G^3/42, & {}_s \varphi_0^4 &= G^2/105 - G^3/77, \\ {}_s \varphi_2^4 &= \sqrt{10} G^2/315 - \sqrt{10} G^3/231, & & \\ {}_s \varphi_4^4 &= \sqrt{70} G^2/630 - \sqrt{70} G^3/462. & & \end{aligned} \quad (12)$$

The curves in Fig. 2 are calculated by substituting the expressions in the system (12) into Eqs. (5)–(7) and they demonstrate the appearance of beats of frequency  $2\omega$  in the intensities  $I_2$  and  $I_3$  and of beats of frequency  $4\omega$  in  $I_1$ . In the latter case there are only oscillations of the hexadecapole moment of the ground state in the linear absorption region. We can see that although beats of frequency  $4\omega$  are very weak, they nevertheless appear in the signal  $I_1$  for the value  $G = 0.5$  used in the calculations, whereas they are practically unnoticeable against the background of quantum beats of frequency  $2\omega$  in the signal  $I_3$ .

## BEATS AFTER ABRUPT ENDING OF PUMPING

Let us assume that pumping sufficiently strong for the orientation of the ground state and acting for a time interval  $\Delta\tau$  considerably greater than the duration of the transient process is suddenly (compare with the characteristic relaxation on  $\gamma^{-1}$ ) switched off at the moment  $t'_0$  (Fig. 1b). In this case the polarization moments in the presence of a strong optical field  ${}_s \varphi_q^\kappa$  are established under steady-state conditions. They can be calculated by numerical solution of the system (10) on the assumption that  $d {}_s \varphi_q^\kappa/dt = 0$ . Then, as shown in Ref. 12, the expressions for the intensity converge

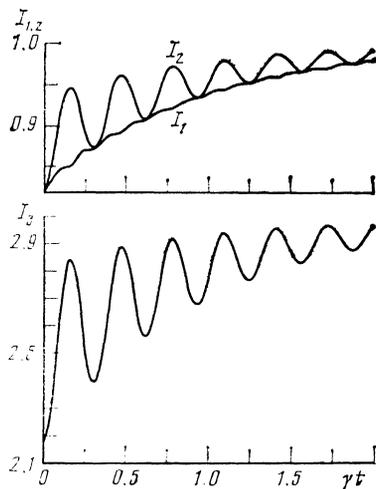


FIG. 2. Beat signals obtained by pumping with a  $\delta$  pulse for different directions and polarization of the observations, calculated for  $G = 0.5$  and  $\omega/\gamma = 10$ .

well even in a strong pump field ( $\Gamma_p/\gamma \sim 10$ ) if the system (10) is truncated for  $\kappa \geq 8$ . A system of equations allowing for reverse spontaneous and stimulated transitions was also solved in Ref. 12. The results of a numerical computer calculation obtained for the geometry in Fig. 1c in the case when  $\Gamma_p/\gamma = 10/3$  are plotted in Fig. 3. The dependences on the ratio  $\omega/\gamma$  are given for the real quantities  ${}_s\varphi_0^x$  (Fig. 3a) and also for the modulus  $\text{mod } {}_s\varphi_q^x$  (Fig. 3b) and the phases  ${}_s\psi_q^x$  (Fig. 3c) of complex polarization moments  ${}_s\varphi_q^x$  with  $q \neq 0$ . The information presented in Fig. 3 makes it possible to reconstruct the kinetics of intensities in a transient process and

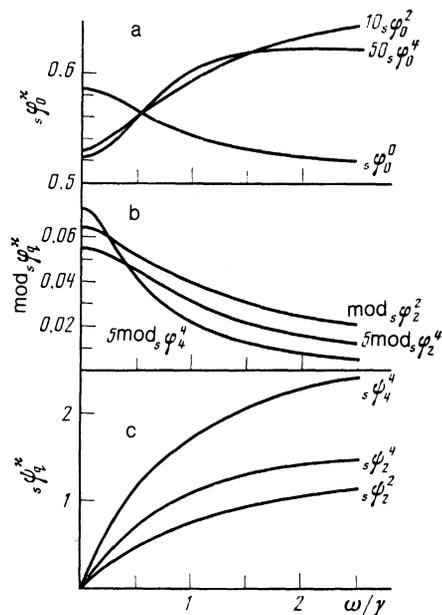


FIG. 3. Dependences of pump-radiation-induced polarization moments of the ground state on the ratio  $\omega/\gamma$ , calculated using Eq. (10) assuming that  $\Gamma_p/\gamma = 10/3$ : a) longitudinal components  ${}_s\varphi_0^x$ ; b) moduli of the transverse components  $\text{mod } {}_s\varphi_q^x \neq 0$ ; c) phases of the transverse components  ${}_s\psi_q^x \neq 0$ .

this can be done using the Eqs. (5)–(7).

We can see from Fig. 3 that the transverse components  ${}_s\varphi_q^x$  with  $q \neq 0$  decay to zero on increase in  $\omega/\gamma$ . Since they are the ones which determine the amplitude of harmonic beats [see Eqs. (5)–(7)], it follows that the beats can be observed only for  $\omega \sim \gamma$ . In fact, if  $\omega \ll \gamma$ , then the transient process ends in a time which is shorter than the beat period, whereas for  $\omega \gg \gamma$  the beat amplitude tends to zero. By way of illustration we shall mention that in the first approximation (with respect to  $\Gamma_p/\gamma$ ) the amplitude of the harmonic component of frequency  $2\omega$  contains a factor  $\Gamma_p/(\gamma^2 + 4\omega^2)^{1/2}$  in the intensity. Consequently, we can in practice expect to detect about one period of oscillations during the transient process, which reduces greatly the opportunity for using a long pump pulse in order to determine the beat frequency. It should be pointed out that the moments  ${}_s\varphi_2^2$ ,  ${}_s\varphi_2^4$ , and  ${}_s\varphi_4^4$  have different oscillation phases (see, the curves for the phases  ${}_s\psi_q^x$  in Fig. 3c), and that the ratio of the phases depends on  $\omega/\gamma$ .

### EXPERIMENTAL RESULTS

Beats associated with the ground state were detected by us in Ref. 10 for the ( $X^1\Sigma_g^+$ ) state of  $K_2$ . Experiments were subsequently carried out in order to determine the dependence of the beat frequency on the magnetic field and use this dependence to calculate the Landé factor. We shall consider briefly the conditions during these experiments. Radiation of 632.8 nm wavelength from a helium-neon laser of the LG-38 type and of about 60 mW power excited the ( $X^1\Sigma_g^+$ , 1.72)  $\rightarrow$  ( $B^1\Pi_u$ , 8.72) transition in  $K_2$  (according to Ref. 15, we should substitute  $J_a'' = J_b' = 73$ , but this aspect is not yet fully understood). Modulation was provided by an ML-102 electrooptic Pockels modulator and by a G5-15 controlled pulse generator. The length of an optical pulse was  $\Delta\tau = 1.8 \mu\text{sec}$  and the growth and decay fronts (leading and trailing edges) were about 300 nsec long (Fig. 4a); the pulse repetition frequency was about 10 kHz. Measurements were made using the  $Q_{16}$  line of a resonance series in the laser-induced fluorescence selected by a DFS-12 monochromator. The line intensities were determined photoelectrically by the photon counting method. The kinetics was determined by the method of delayed coincidences, using a time-amplitude transducer in the start-stop regime<sup>16</sup> and an AI-256-6 pulse analyzer.

Figure 4b shows the kinetics of the intensity  $I_3$  in the absence of a magnetic field, whereas Fig. 4c gives the same kinetics in a field  $B = 0.816$  T applied in the geometry of Fig. 1c. A magnetic field was created by a Hall sensor calibrated by the NMR method. In an analysis of the signals a correction was made for the profile of the exciting pulse (Fig. 4a) and also for distortions because the conditions for one-photon statistical analysis<sup>17</sup> were not fully satisfied in the start-stop regime. The signals were normalized to unity at the end of the selected time interval. The observation geometry corresponding to  $I_3$  was selected deliberately (Fig. 1c), because in this case we could expect the maximum amplitude of quantum beats of frequency  $2\omega$  to have a three times as high total intensity (Fig. 2), and the influence of beats of frequen-

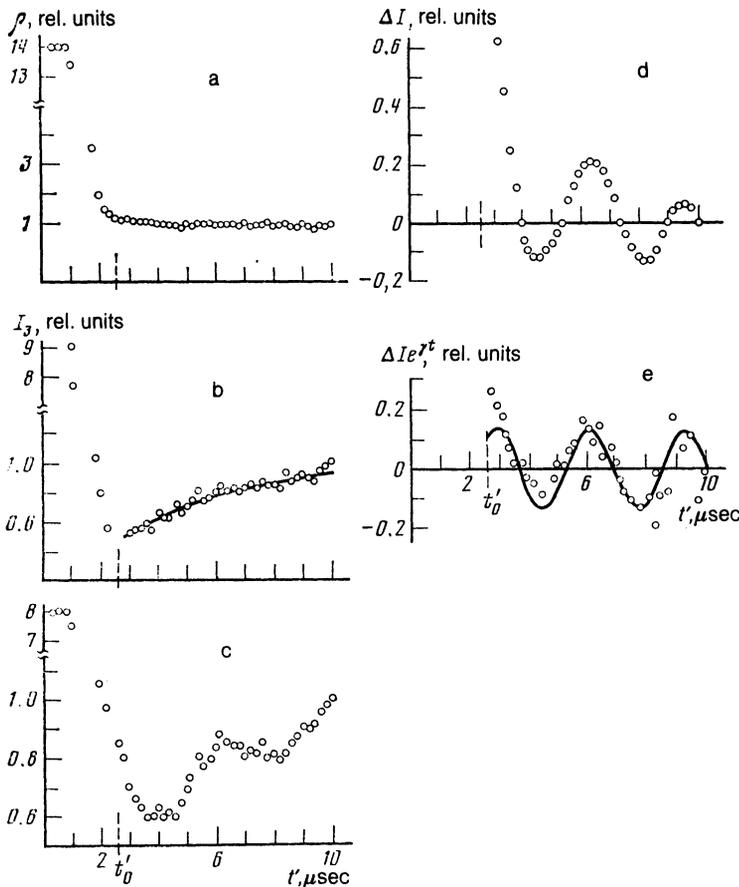


FIG. 4. Experimentally recorded signals for the ( $X^1\Sigma_g^+$ ) state of  $K_2$  at  $T = 441$  K: a) optical pump pulse; b) kinetics of the laser-induced fluorescence in the absence of a magnetic field; c) kinetics of the same fluorescence in a field of  $B = 0.816$  T; d) difference signal after smoothing out; e) difference signal corrected for the decay of the  $\beta$  amplitude. The values for every fifth pulse analyzer channel are shown.

cy  $4\omega$  was negligible. Clearly, instead of a monotonic rise of the intensity of application of a magnetic field, a harmonic component was observed and this should correspond to quantum beats of the lower state of frequency  $2\omega$ .

A clear demonstration of beats in Fig. 4d in accordance with Eq. (7) revealed the difference between the signals shown in Fig. 4c and characterized by  $\omega \neq 0$  and those in Fig. 4b characterized by  $\omega = 0$ , flattened by the method of the average value with a window about 20 channels wide.

We shall now describe the proposed method of obtaining data from the recorded signals. It should be mentioned that in the case of an excited state ( $B^1\Pi_u$ ) of  $K_2$  a typical decay rate should be  $\Gamma \approx 10^8 \text{ sec}^{-1}$ , considerably greater than the rate of relaxation of  $\gamma$  between  $v'', J''$  in the ground electronic state  $X^1\Sigma_g^+$ , which is a quantity of the order of  $10^6 \text{ sec}^{-1}$  (see, for example, Fig. 4b). Hence, bearing in mind that the pumping rate is  $\Gamma_p \ll \gamma$ , we find that these approximations provide a satisfactory answer and they have been used in Eqs. (5)–(7) and (10). However, the expressions in Eq. (12) are satisfied less well since the width of a pump pulse  $\Delta\tau = 1.8 \mu\text{sec}$  was not sufficiently small compared with  $\gamma^{-1} = 4 \mu\text{sec}$ , and, moreover, it was difficult to estimate the error represented by the solution of Eq. (11) to within  $G^3$  for the experiments under discussion. In the case when  $\Delta\tau \ll \gamma^{-1}$ , the substitution of Eq. (12) into Eq. (6) would have made it possible to determine from the experimental results the values of  $\omega$  and  $\gamma$ , the pumping parameter

$G$ , and the contribution of each of the polarization moments to the signal. In our case we can consider only the problem of determination of the beat frequency  $2\omega$  and of the relaxation rate  $\gamma$ . Ignoring quantum beats characterized by  $4\omega$ , we can represent the laser-induced fluorescence signal in the form

$$I(t) = I(\infty) - C_1 e^{-\gamma t} + C_2 \cos(2\omega t + \psi) e^{-\gamma t}, \quad (13)$$

where  $t = t' - t'_0$ ;  $C_i$  are constants;  $\psi$  is the phase introduced because of the finite width of the pump pulse. We first analyzed signals with  $B = 0$ , i.e., those with  $\omega = 0$ , and found the value of  $\gamma$  by variation of the nonlinear parameter in Eq. (13). For example, for the signal in Fig. 4b we found that  $\gamma = 0.25 \times 10^6 \text{ sec}^{-1}$ .

Determination of the frequency  $2\omega$  under conditions of a noisy signal and manifestation of a small number (of the

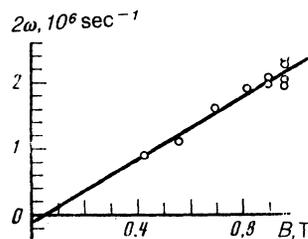


FIG. 5. Dependence of the frequency of quantum beats  $2\omega$  on the magnetic field  $B$ .

order of one) of periods during the characteristic decay time of the amplitude  $\gamma^{-1}$  was a difficult task. We used the difference signal between the values for  $B \neq 0$  and  $B = 0$  (Figs. 4b and 4c), corrected for the decay using  $\exp(\gamma t)$  where the known value of  $\gamma$  was substituted. An example of such a signal is shown in Fig. 4e; no smoothing out procedure was applied to this case. This procedure had the advantage that the frequency  $\omega$  could be determined by minimization of just one nonlinear parameter by writing down first  $\cos(2\omega + \psi)$  in terms of a sum of trigonometric functions of the arguments, so that the phase  $\psi$  occurred in the form of linear cofactors. The curve calculated in this way is shown in Fig. 4e. An analysis showed that it was undesirable to use all the available values of  $I(t)$ , because the exponential decay of the beat amplitude resulted in a situation in which the last channels carried practically no information on the harmonic component, but simply increased the error. Selection of the optimal number of channels was made by an analysis of the behavior of the sum of the squares of the deviations on the basis of the criterion of the sharpest minimum in its dependence on  $\omega$ .

The values of  $2\omega$  obtained in this way are plotted in Fig. 5 for different values of the magnetic field. The straight line found by minimization passed, within the limits of the experimental error, through the origin, exactly as expected. The slope of the straight line gave the value of the Landé factor for the EVR level ( $X^1\Sigma_g^+$ , 1.72) of  $K_2$  which was  $g_a = (1.30 \pm 0.27) \times 10^{-5}$  for the confidence limit of 0.95. The value of the Landé factor just quoted agreed, within the limits of the error, with the  $g_a = (0.99 \pm 0.05) \times 10^{-5}$  given in Ref. 9 and obtained by the method of a nonlinear resonance with the beats for the same EVR level of  $K_2$ , and with the value of  $1.177 \times 10^{-5}$  obtained in Ref. 18 by the *rf* resonance method in a molecular beam for the whole ( $X^1\Sigma_g^+$ ) state of  $K_2$  in thermal equilibrium. The considerable error in the present study was due to an insufficiently large value of the ratio  $\omega/\gamma$ , which could not be increased by increasing the magnetic field intensity because of the limitations of the magnet used in our experiments. Moreover, it should be possible to increase also the ratio of the signal to the noise in the

process of recording the signal. One may assume after overcoming these experimental difficulties the proposed method will become the most precise technique for the investigation of the magnetism of the ground state of molecules, because it combines selectivity in respect of the vibrational-rotational sublevels with the absence of nonlinear distortions of the signal.

A reduction in the statistical scatter should also make it possible to detect beats of frequency  $4\omega$ , which could be done using the signal  $I_1$  (see Figs. 1c and 2).

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