Resonance of quantum beats in a system of magnetic sublevels of the ground electronic state of molecules

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Theoretical and experimental investigations were made of a nonlinear resonance of quantum beats in the ground electronic state of gaseous molecules, which were observed when the frequency of harmonic modulation of laser pump radiation was equal to the splitting frequency of the Zeeman sublevels between which coherence was established in the course of absorption. The two-level approximation was employed in the range of large values of the angular momentum $J \gg 1$ to develop a semiclassical description of the effect and to calculate the beat resonance signals in the degree of polarization of laser-excited fluorescence allowing for the real mode structure of the exciting laser radiation in the form of a set of longitudinal modes. The validity of the approximation of a wide excitation line, a nonlinear shift of the position of the resonance, and a shift due to the influence of the Zeeman splitting of the excited state were considered. The experiments were carried out on a $^{39}K_2$ molecule $(X\,^1\Sigma_g^+, v'', J'')$ pumped optically by the 632.8 nm line of an He-Ne laser. An analysis of the experimentally recorded signals within the framework of the semiclassical description made it possible to determine the Landé factor for a vibrational–rotational level with $v'' = 1, J'' = 73$ and this factor was found to be $(1.01 \pm 0.03) \times 10^{-5}$.

INTRODUCTION

Quantum beats are due to interference of quantum states of an ensemble of particles (for reviews, see Refs. 1 and 2). A resonance of beats of interfering states occurs when the frequency of their splitting is equal to the frequency of periodic modulation of a light field inducing optical transitions. The effect can be used to directly measure the splitting of adjacent levels and is essentially one of the high-resolution spectroscopic techniques free of the Doppler broadening. The phenomenon of a beat resonance has been investigated thoroughly in the case of excited states of the atoms when detection usually involves a resonant change in the amplitude of a modulated fluorescence signal if the modulation frequency of the excitation is equal to the splitting frequency of the interfering sublevels. It would be of interest to extend the beat resonance method to molecular systems. In the case of electronically excited states linked by optical transitions to the ground state there are no fundamental differences from atomic systems. In particular, it is possible to record resonance series by the method of laser-excited fluorescence (for a monograph, see Ref. 3).

The situation is much more complex in the case of the ground electronic state of molecules when, as shown in Ref. 4, we can use a nonlinear variant of the beat resonance effect, particularly the resonance between magnetic sublevels M'' of an electronic-vibrational-rotational (EVR) level with quantum numbers α'', v'', and J''. In this case the coherence between the magnetic sublevels is created by the light field as a result of optical clearing of the lower level in the course of absorption of radiation by a molecule (this is called optical pumping in Ref. 5). The same field transfers the coherence of the magnetic sublevels of the ground state to higher states and this is manifested in the fluorescence.

The main methodological value of this beat resonance variant is the opportunity to determine accurately the Landé factor, which is very important for a diamagnetic ground electronic state because we can then estimate the hyperfine structure constants, judge the interaction between the terms, etc. However, in view of the influence of the excited states and nonlinear shifts of the position of a resonance in the presence of a strong field, the precision of the determination of the Landé factor depends largely on the correctness of the theoretical description. A description obtained using the polarization moment employed earlier in Refs. 4 and 6 makes it possible to derive an analytic expression for the beat resonance signal. However, the approximation of an expansion series in terms of the intensity of the optical field is too rough and, in particular, it ignores the nonlinear shift. On the other hand, a description based on the model of classical dipole oscillators used in Ref. 7 ignores stimulated and reverse spontaneous transitions to the level just emptied and it is therefore limited to the case of linearly polarized pumping; moreover, considerable computer time is needed in the calculations, so that this approach is not very productive in the analysis of the experimental data in which parameters are varied. Moreover, the problem of the real mode composition of the exciting laser radiation remains unsolved.

We shall provide a description of a nonlinear beat resonance of molecules using the apparatus of the classical description of the orientation of the angular momentum of a molecule in the case when $J \gg 1$. We shall formulate and solve the kinetic equations which allow for the mode composition of a laser. We shall report an experiment on the K_2 molecules carried out in order to test whether the theoretical description is satisfactory and to obtain a more accurate value of the Lande factor of the EVR level of K_2 $(X\,^1\Sigma_g^+, v'', J'')$.

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DESCRIPTION OF THE METHOD

Let laser radiation induce an optical transition $a \rightarrow b$ (Fig. 1a) at a rate Γ_p. Then, the probability of filling of the initial level a by reverse spontaneous transitions $b \rightarrow a$ is low, which is typical of molecules in which an unexcited electronic state splits into a large number of EVR levels and the main process which fills the level a is nonradiative relaxation characterized by a constant Γ_a. If $\Gamma_p \gtrsim \Gamma_a$, effective optical clearing of the level a occurs and because of the selectivity of the absorption in respect of M'', an anisotropic distribution of the magnetic sublevels is established. This optical alignment or orientation of the lower level is manifested by changes in the intensity and degree of polarization of fluorescence. In the case of linearly polarized excitation the degree of polarization of such fluorescence is described by $P = (I_\parallel - I_\perp)/(I_\parallel + I_\perp)$, where $I_\parallel$ and $I_\perp$ are the fluorescence intensities (for example, as a result of the $b \rightarrow c$ transition, see Fig. 1a) for parallel ($I_\parallel$) and orthogonal ($I_\perp$) polarizations relative to the polarization of the exciting light beam (Fig. 1b). In the case of weak excitation ($\Gamma_p \ll \Gamma_a$, Γ_b) for a Q-type transition, the degree of polarization is $P = 0.5$ and an increase in Γ_p reduces P (Fig. 1c). We shall assume that an external magnetic field $\mathbf{B} \perp \mathbf{E}$ is applied to the system of molecules (Fig. 1b). If the condition $\omega_a/\Gamma_a \gg \omega_b \Gamma_b$ is satisfied, where $\omega_{a,b} = g_{a,b}\mu_0 B/\hbar$ is the precession frequency, $g_{a,b}$ is the Landé factor of the level a or b, and Γ_b is the rate of decay of the upper level, then an increase in the field B first activates the Hanle effect in the case of the lower level because of the loss of coherence induced by the radiation between the magnetic sublevels,[8] which increases P (Fig. 1c), and then depolarization occurs because of the Hanle effect of the excited state b.

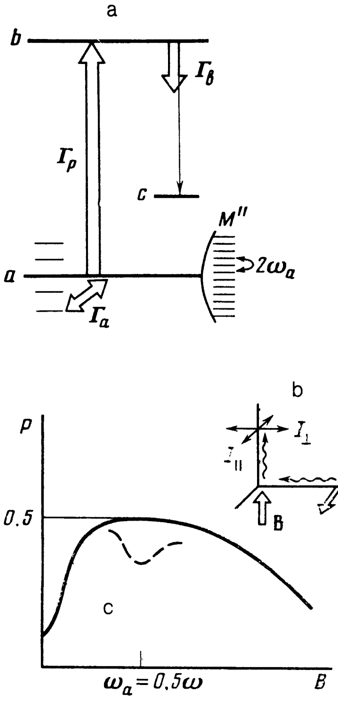

FIG. 1. Schematic diagram showing optical pumping (a, b) and the characterisic dependence of the decay of polarization P of the fluorescence on the magnetic field (c).

We shall assume that the absorption rate Γ_p is amplitude-modulated at the frequency ω, i.e., $\Gamma_p = \Gamma_{p0}(1 + \varepsilon \cos \omega t)$ and ε is the depth of modulation. When ω coincides with the splitting frequency of the magnetic sublevels ($|\Delta M''| = 2$), the coherence destroyed by the magnetic field is restored and this is manifested in the excitation scheme in Figs. 1a and 1b as a resonant reduction in the degree of polarization with a minimum near $\omega = 2\omega_a$ (dashed curve in Fig. 1c). This signal is the manifestation of a nonlinear beat resonance between the magnetic sublevels of the lower level a. It should be stressed that in this case a beat resonance is observed for time-averaged, i.e., steady-state, recording of $I_{\parallel,\perp}$.

In the experiment described below it was more convenient to determine the dependence of the intensity and of the degree of polarization of laser-induced fluorescence on the modulation frequency for a fixed value of an external magnetic field.

EXPERIMENT

We investigated the $^{39}K_2$ molecule and used the 632.8 nm line of a helium-neon laser to excite strongly several EVR transitions in the X-B band. We used the strongest EVR transition of the Q type ($X'\Sigma_g^+$, $v'' = 1$, $J'' = 73) \rightarrow (B\,^1\Pi_u, v' = 8, J' = 73)$; the identification of the quantum numbers of the transition follows Ref. 9. A laser of the LG-38 type with an output power of about 60 mW (average power density 2 W/cm^2) generated many longitudinal modes separated by an intermode spacing $\Delta\omega_L = 470$ MHz, so that within the limits of the Doppler absorption profile of the K_2 molecule (at a temperature of $T = 450$ K) it was possible to fit approximately 11 modes. Frequency stabilization of the laser was not attempted.

Saturated potassium vapor filled a cylindrical glass cell 20 mm in diameter connected to a vacuum system which ensured that the residual pressure did not exceed 5×10^{-6} Torr. The working temperature of a stub containing metallic potassium was kept constant in a thermostat at 441 K, which corresponded to the concentrations $[K] = 0.30 \times 10^{14}$ cm^{-3} and $[K_2] = 0.13 \times 10^{11}$ cm^{-3} of the potassium atoms and molecules, respectively.[10]

At these vapor concentrations it was found in Refs. 11 and 12 that the relaxation rate Γ_a of the lower level was governed both by K_2-K collisions causing transitions in a system of vibrational-rotational levels, and by collisionless relaxation due to the loss of molecules from the zone of the exciting beam and arrival in this zone of molecules in thermal equilibrium from other parts of the cell (transit relaxation). In view of the large number of the vibrational-rotational levels within the limits of kT from the level being cleared, which were participating in the relaxation processes (Fig. 1a), it was permissible to assume that they were practically unaffected by optical pumping and acted as a kind of thermal reservoir. Estimates of the values of the parameters $\Gamma_{p0} \sim \Gamma_a \sim 10^6$ sec^{-1} (Ref. 11) indicated that the induced b→a transitions played a very small role since the spontaneous decay time of K_2 ($B\,^1\Pi_u, v' = 8, J' = 73$) was $\tau_{sp} = 11.6$ nsec (Ref. 8). Under the experimental conditions we could ignore collisional processes involving the excited state $B\,^1\Pi_u$ and assume that the homogeneous half-width Γ_{ab} of the $a \rightarrow b$ transition satisfied the relationship $\Gamma_{ab} = \tau_{sp}^{-1}/2 = \Gamma_b/2$.

A laser beam was modulated by an electrooptic ML-102 modulator based on the Pockels effect, which was controlled by a high-power GZ-41 generator of sinusoidal signals, the frequency range of which was extended somewhat toward lower frequencies. The amplitude of the sinusoidal voltage was about 60 V. The depth of modulation of the exciting pulse was $\epsilon = 0.8$; the modulation frequency was measured with a ChZ-54 meter. Part of the exciting light was deflected to an FD-24 photodiode in order to provide visual control of modulation. The laser beam was reflected from a mirror and passed twice through a fluorescence cell in order to increase the pumping efficiency Γ_{p0}/Γ_a.

The fluorescence measurements were made for the Q_{16} line of the resonance series corresponding, according to Ref. 9, to the Q transition $B\,'\Pi_u\,(8,73)\rightarrow X\,^1\Sigma_g^+\,(16,73)$. This line was selected by a DFS-12 double monochromator with a reciprocal dispersion 0.5 nm/mm. An optical system with a rotatable mirror and with spherical and cylindrical lenses focused the luminous region onto the entry slit of the DFS-12 mono-chromator. The rotatable mirror and a cell placed inside a furnace were located between the poles of an electromagnet in such a way that observations were made along the direction of a magnetic field **B**. The field created by the electromagnet was 0.8 T when the gap was 40 mm. The value of B was measured with a Hall probe calibrated using an NMR magnetometer with a total error of about 2%. The entry slit was divided by a vertical line into two parts and these parts were covered by polaroids with orthogonal orientations transmitting $I_\parallel$ and $I_\perp$. The fluorescence emerging from the corresponding parts of the exit slit was guided by fibers to two FÉU-79 photomultipliers. Then, two channels were used to record simultaneously one-electron pulses which were accumulated in two ChZ-38 counters. In this way it was possible to record simultaneously the intensities $I_\parallel$ and $I_\perp$ in two channels (Fig. 1b) and thus find the value of P. The channels were calibrated to ensure equal intensities for rotation of the vector **E** exciting light along the field **B**. However, the optical channel as a whole resulted in some depolarization of the laser-induced fluorescence. The normalization coefficient C_{dep} was determined to allow for such depolarization by recording the dependence P(B) similar to that shown in Fig. 1(c), which under these conditions represented the superimposed Hanle signal of the ground and excited states.[8] The dependence was approximated by a curve calculated assuming that the values of ω_a, ω_b, and Γ_b were known and varying the parameters Γ_{p0}, Γ_a, and the linear parameter C_{dep}. This procedure made it possible to find the normalization coefficient C_{dep} by which the experimentally determined values of P should be multiplied in order to compensate for the depolarization factors. The values of C_{dep} were found to be about 1.05. The values of Γ_{p0} and Γ_a were also useful as the starting data in the minimization of the beat resonance signals.

A typical beat resonance signal recorded using the coordinates P and $\omega/2\pi$ is shown in Fig. 2a (in a magnetic field $B = 0.589$ T). The next task was a theoretical description of the signal obtained under our experimental conditions.

DESCRIPTION OF THE SIGNAL

The intensity of the fluorescence due to the $b\rightarrow c$ transition is known to depend on the population, orientation, and alignment of the level b. It follows from the above model that we can find these characteristics by solving a two-level problem corresponding to the $a\rightarrow b$ transition (see Fig. 1a). Since the angular momentum obeys $J \gg 1$ it is convenient to adopt the Wigner or $\vartheta\varphi$ representation within the framework of which the orientation of the angular momentum can be described semiclassically.[13,14] In the case of the matrix elements $f\,(J_iM_i\,|J_kM_k\,)$ of an arbitrary operator written in the M representation a transition to $\vartheta\varphi$ is made by the transformation[14]

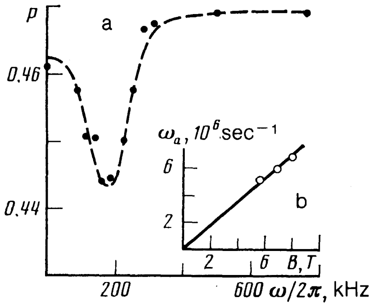

FIG. 2. a) Results of an experimental determination of the degree of polarization P (black dots) compared with the theoretical dashed curve calculated in the wide line approximation on the assumption that $\Gamma_a = 0.131\times 10^6$ sec^{-1}, $\omega_a = 0.352\times 10^6$ sec^{-1}, $\Gamma_b = 86.2\times 10^6$ sec^{-1}, $\omega_b = 9.843\times 10^6$ sec^{-1}, and $\Gamma_{p0} = 0.813\times 10^6$ sec^{-1}. b) Dependence of ω_a on the magnetic field B.

$$f_{ik}(\vartheta\varphi)=\sum_{\Delta M}\exp(i\varphi\Delta M)f\left(J_i\bar{M}+\frac{\Delta M}{2}\,\middle|\,J_k\bar{M}-\frac{\Delta M}{2}\right), \qquad (1)$$

where

$$\cos\vartheta\equiv 2\bar{M}/(J_i+J_k+1),$$

and the angles ϑ and φ represent the orientation of the angular momentum.

If we apply the transformation of Eq. (1) to the equations for the density matrix ρ in the M representation and retain only the terms of the zeroth order in terms over a small parameter $1/J$, we obtain

$$\frac{\partial}{\partial t}\rho_{aa}+\mathbf{v}\frac{\partial}{\partial\mathbf{r}}\rho_{aa}+\omega_a\frac{\partial}{\partial\varphi}\rho_{aa}+i(V_{ba}\rho_{ab}-\rho_{ba}V_{ab})+\Gamma_a\rho_{aa}=\Gamma_a\bar{\rho}_{aa},$$

$$\frac{\partial}{\partial t}\rho_{ab}+\mathbf{v}\frac{\partial}{\partial\mathbf{r}}\rho_{ab}+i\Delta\omega_{ab}J\cos\vartheta\rho_{ab}$$

$$+\bar{\omega}_{ab}\frac{\partial}{\partial\varphi}\rho_{ab}+iV_{ba}(\rho_{aa}-\rho_{bb})+\Gamma_{ab}\rho_{ab}=0,$$

$$\frac{\partial}{\partial t}\rho_{bb}+\mathbf{v}\frac{\partial}{\partial\mathbf{r}}\rho_{bb}+\omega_b\frac{\partial}{\partial\varphi}\rho_{bb}+i(V_{ab}\rho_{ba}-\rho_{ab}V_{ba})+\Gamma_b\rho_{bb}=\Gamma_b\bar{\rho}_{bb},$$

$$\rho_{jk}=\rho_{jk}(\vartheta\varphi), \qquad V_{jk}=V_{jk}(\vartheta\varphi)$$

$$(j,\ k=a,\ b), \quad J=(J_i+J_k+1)/2,$$

$$\Delta\omega_{ab}=\omega_a-\omega_b, \quad \bar{\omega}_{ab}=(\omega_a+\omega_b)/2, \quad \Gamma_{ab}=(\Gamma_a+\Gamma_b)/2. \qquad (2)$$

Here, $\bar{\rho}_{aa}$ and $\bar{\rho}_{bb}$ are the equilibrium populations of the upper and lower states. The system of Eq. (2) is written down in a coordinate system in which the z axis is directed along the magnetic field.

The matrix element of the dipole interaction in the $\vartheta\varphi$ representation is

$$V_{ab}=-\sum_{\sigma}\frac{d_{ab}E_{\sigma}D^{1*}_{\sigma\Delta J}(\varphi,\vartheta,0)}{2\hbar(J_a+J_b+1)^{1/2}}, \tag{3}$$

where

$$\Delta J=J_a-J_b,$$

d_{ab} is the reduced matrix element of the dipole moment, E_σ are the circular components of the electric field vector of the wave, and D^1 is the Wigner rotation matrix. In the case of a Q-type transition the degree of polarization P of the fluorescence can be expressed in terms of ρ_{bb} as follows:

$$P=\int d\cos\vartheta\, d\varphi \cos^2\vartheta \cos 2\varphi\langle\rho_{bb}\rangle_{v,t}\times\left\{\int d\cos\vartheta\, d\varphi\cos^2\vartheta\langle\rho_{bb}\rangle_{v,t}\right\}^{-1}, \tag{4}$$

where $\langle\rho_{bb}\rangle_{v,t}$ represents averaging over the velocities characterized by a Maxwellian distribution and also averaging with respect to time.

The system of Eq. (2) can be simplified if it is reduced to two equations for the diagonal elements of the density matrix. Then, the formal solution for an off-diagonal element

$$\rho_{ba}(t,\vartheta,\varphi)=-i\int_0^\infty d\tau \exp[-\tau(\Gamma_{ab}+i\mathbf{kv}+\Delta\omega_{ab}J\cos\vartheta)][V_{ba}(\rho_{aa}-\rho_{bb})]_{t-\tau,\vartheta,\varphi-\overline{\omega}_{ab}\tau} \tag{5}$$

can be substituted into the equations for the diagonal elements. Equation (5) allows for the spatial dependence ($\propto \exp i\mathbf{kr}$) of the matrix element of the interaction. Since under the experimental conditions we have $\Gamma_{p0}\ll\Gamma_{ab}$, it follows that $|V_{ab}|^2/\Gamma_{ab}\Gamma_a\ll 1$, so that in the integrand of Eq. (5) we can ignore the term ρ_{bb} and we can take ρ_{aa} outside the integral and assume that its value is that at the point $\tau=0$ in view of the smallness of the variation of ρ_{aa} on the time scale $1/\Gamma_{ab}$. This is valid if $\overline{\omega}_{ab}$, $\Gamma_a\ll\Gamma_{ab}$.

We shall also bear in mind that the laser radiation represents in fact a set of longtudinal modes, i.e., that V_{ab} can be represented by

$$V_{ab}(t)=\Sigma V_{ab}^{i}\exp(i\Omega_i t),$$

where Ω_i is the frequency of the i-th mode. Since the experimental conditions indicate that $\Omega_i-\Omega_{i-1}=\Delta\omega_L\gtrsim\Gamma_{ab}$, it follows that in the equations for the diagonal elements we can also ignore the rapidly oscillating components of the dynamic term, which are multiples of the frequency $\Delta\omega_L$. This gives

$$\begin{gathered}\frac{\partial}{\partial t}\rho_{aa}+\omega_a\frac{\partial}{\partial\varphi}\rho_{aa}+(\Gamma_a+\tilde{\Gamma}_p)\rho_{aa}=\Gamma_a\bar{\rho}_{aa},\\ \frac{\partial}{\partial t}\rho_{bb}+\omega_b\frac{\partial}{\partial\varphi}\rho_{bb}-\tilde{\Gamma}_p\rho_{aa}+\Gamma_b\rho_{bb}=\Gamma_b\bar{\rho}_{bb},\end{gathered} \tag{6}$$

$$\tilde{\Gamma}_p=\sum_i\frac{2\Gamma_{ab}|V_{ba}^{i}|^2}{\Gamma_{ab}^2+(J\Delta\omega_{ab}\cos\vartheta+\mathbf{kv}+\Omega_i)^2}=\frac{2d_{ba}^2\left|\sum_\sigma e_\sigma D^{1*}_{\sigma\Delta J}(\varphi,\vartheta,0)\right|^2}{4\hbar^2(J_a+J_b+1)}\times\sum_i\frac{\Gamma_{ab}I_i}{\Gamma_{ab}^2+(J\Delta\omega_{ab}\cos\vartheta+\mathbf{kv}+\Omega_i)^2}. \tag{7}$$

Here, $I_i=\Sigma_\sigma|E_{i\sigma}|^2$ and e_σ are the cyclic components of a unit polarization vector. In the case when all the values of I_i are the same, Eq. (7) can be written in the form

$$\tilde{\Gamma}_p=\Gamma_p\left|\sum_\sigma e_\sigma D^{1*}_{\sigma\Delta J}(\vartheta,\varphi,0)\right|^2\times\sum_i\frac{\Gamma_{ab}}{\Gamma_{ab}^2+(J\Delta\omega_{ab}\cos\vartheta+\mathbf{kv}+\Omega_i)^2}, \tag{8}$$

where Γ_p is a quantity which is frequently called the pumping rate (see, for example, Ref. 5). Similar equations were first derived by Ducloy[13] using representation of coherent states. Ducloy employed the approximation of a wide luminescence line (see Ref. 15). This corresponds approximately to the sum over i in the expression for $\tilde{\Gamma}_p$ being replaced formally with I_λ, which is the spectral density of the radiation intensity. The conditions of validity of the wide line approximation are that the total width of the spectrum of the exciting radiation is considerably greater than Γ_{ab} and the spectrum itself is either continuous or consists of spectral components separated by intervals much smaller than Γ_{ab}. In particular, it follows from Eq. (7) for $\tilde{\Gamma}_p$ that if $\Delta\omega_L\ll\Gamma_{ab}$, the sum over the modes can be replaced with an integral and the condition of a large spectral width is ensured by continuous variation of I_i on the Γ_{ab} scale. Consequently, when these two conditions are satisfied in Eqs. (6) and (7), we obtain the wide line approximation. It should be pointed out that in the case of this approximation we can include also the saturation effects in the $a\to b$ transition, i.e., the equations in the wide line approximation remain valid when we make the substitution $\rho_{aa}\to\rho_{aa}-\rho_{bb}$ in the terms proportional to $\tilde{\Gamma}_p$ in Eq. (6) (see Ref. 13). Since under experimental conditions we have $\Gamma_{ab}<\Delta\omega_L$, it is strictly speaking not possible to use the wide line approximation and one should employ a more general expression for $\tilde{\Gamma}_p$ given by Eq. (7).

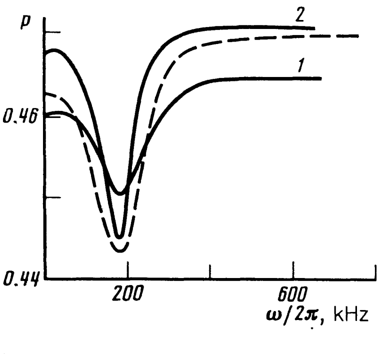

FIG. 3. Wide line approximation curve (dashed) and curves calculated using Eq. (7): 1) $\Gamma_a=0.262\times10^6$ sec^{-1}, $\Gamma_{p0}=0.4\times10^6$ sec^{-1}; 2) $\Gamma_a=0.655\times10^5$ sec^{-1}, $\Gamma_{p0}=0.5\times10^6$ sec^{-1}.

RESULTS OF CALCULATIONS

We shall solve the system of equations (6) for harmonically modulated excitation $\Gamma_p=\Gamma_{p0}(1+\varepsilon\cos\omega t)$. We shall expand the density matrix as a two-dimensional Fourier series

$$\rho=\sum_{k,l}\rho^{k,l}(\vartheta)\exp(i\varphi k+il\omega t). \tag{9}$$

Consequently, we obtain a linear system of algebraic equations for the Fourier components $\rho^{k,l}$. Equations of this type are encountered in numerical solutions of differential equations by the finite difference methods. Therefore, in this case we can use the well-known iteration methods for the solution of equations, such as the Seidel method.[16] In solving the equations a limited number of the components k, l was selected. A satisfactory accuracy for the selected relaxation coefficients and Γ_p was achieved already for $|k|$, $|l|\leqslant 10$. The solution found for $\rho_b^{k,l}$ was used to calculate the intensity and the degree of polarization of the fluorescence from Eq. (4). Since in the experiments the intensity of the recorded fluorescence was averaged in time, only the harmonic $l=0$ contributed to Eq. (4). Multiple integrals in Eq. (4) were calculated by the Korobov method.[17]

A numerical solution of the system of equations (6) and selection of the constants Γ_c and ω_a, and of the laser radiation intensity, were used to find the $P(\omega)$ curve which agreed best with the experimental results. Although, as pointed out above, the wide line approximation was inapplicable, the best agreement between the numerical calculations and the experimental results was obtained, surprisingly enough using this approximation (dashed curve in Fig. 2a). However, when Eq. (7) was used for the dynamic term, it was not possible to obtain simultaneously the required depth and width of a resonance dip. Figure 3 shows, by way of example, the curves obtained for several values of the parameters illustrating this circumstance. One of the possible explanations is that the wide line approximation operates well in spite of the fact that the conditions of its validity are no longer satisfied because if a laser is not stabilize its modes drift on the frequency scale and such a drift justifies the wide line approximation. The laser instability can be allowed for in Eqs. (6) and (7) by assuming that $\Omega_i=\Omega_i(t)$. In our calculations we used a specific dependence $\Omega_i(t)=\Delta\omega_L(i+t/T)$. In view of the periodicity of the mode pattern on the frequency scale when this dependence $\Omega_i(t)$ was used, the dynamic term in the system (6) became a two-period function of time: one period $(2\pi/\omega)$ was due to modulation of the laser radiation and the other period (T) was due to instability of the mode pattern of the laser radiation.

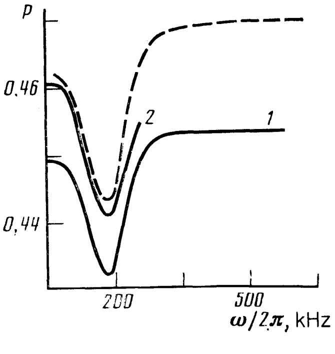

FIG. 4. Curves calculated using Eq. (4) for the same parameters as in Fig. 2a; 1) without allowance for mode drift; 2) assuming that $T=1.85\times10^{-6}$ sec. The dashed curve is obtained in the wide line approximation.

Figure 4 shows several $P(\omega)$ curves obtained for different values of T, but the same parameters Γ_a, Γ_b, ω_a, ω_b, and Γ_{p0} which ensured the best agreement with the experimental points within the wide line approximation. Curve 1 corresponds to the absence of mode drift. For $T=1.85\times10^{-6}$ sec (curve 2), the calculated results approach much closer the curve obtained on the basis of the wide line approximation and finally for $T=0.46\times10^{-6}$ sec the calculated and experimental result agree practically completely. This is to be fully expected on the basis of the physical considerations. If the mode drift is sufficiently rapid compared with the rate of relaxation of the Bennett dips in the ground state ($2\pi/T\gg\Gamma_a$), the saturation in respect of the velocities becomes uniform and this is typical of a continuous spectrum (wide line approximation). Since we used a laser without frequency stabilization or mode locking, mode drift did occur and we could not exclude the possibility that this drift gave rise, at least partly, to an excitation homogeneous in respect of the velocities and typical of the wide line approximation.

We shall now draw attention to the circumstance that, irrespective of the analysis methods described above, the position of the minimum of the dip in the $P(\omega)$ graph is located at the same value of ω (Figs. 3 and 4). This means that the wide line approximation firstly describes correctly the qualitative features of a beat resonance and, secondly, makes it possible to determine quite reliably the value of the g factor of the lower level.

Curves similar to that shown in Fig. 2a were recorded for three different values of the magnetic field. We then found that ω_a obtained in this way fitted a straight line $\omega_a=g_aB\mu_0/\hbar$ (Fig. 2b) and gave $g_a=(1.01\pm0.03)\times10^{-5}$ for the $K_2(X^1\Sigma_g{}^+$, $v''=1$, $J''=73)$ state. The value obtained was found to be very close to the preliminary result $(0.99\pm0.05)\times10^{-5}$ from Ref. 6. It was slightly less than 1.177×10^{-5} given in Ref. 18, which was determined by the method of molecular beams for the whole $K_2(X^1\Sigma_g{}^+)$ state. It should be pointed out that the Landé factor found in the present state was subject to a much smaller error than in Ref. 20, where the method of recording quantum beats in the kinetics of a transient process was used under pulsed optical clearing of the lower EVR level and the value $(1.30\pm0.27)\times10^{-5}$ was obtained.

We can readily see from Fig. 2a that our value of g_a is close to that obtained from the modulation frequency $\omega_{\min}$ corresponding to the position of the minimum if we use the formula $g_a=\hbar\omega_{\min}/2\mu_0B$. However, this agreement is to some extent accidental. In reality, the position of the minimum may be shifted in one or the other direction, as pointed out already in Refs. 7 and 19. The approach developed here allowed us to analyze possible shifts for different values of the parameters governing the $P(\omega)$ curve and for different types of transitions. Moreover, the $P(\omega)$ curve could manifest additional extrema, particularly that associated with a beat resonance between the magnetic sublevels characterized by $|\Delta M''|=4$, as reported in Ref. 6.

Special careful measurements carried out by us in the modulation frequency range near $\omega=4\omega_a$ again confirmed the existence of a small additional maximum. An analysis of the appearance of this maximum in the calculated curves is given below.

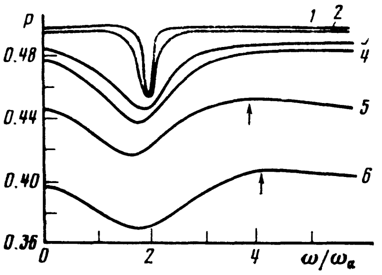

FIG. 5. Beat resonance signals calculated in the wide line approximation for $\varepsilon = 0.8$, $\omega_b = 0$, $\Gamma_a = 3\times10^5$ sec^{-1}, $\Gamma_{p0}/\Gamma_a = 100/3$ and different values of ω_a (sec^{-1}): 1) 10^8; 2) 3×10^7; 3) 10^7; 4) 8×10^6; 5) 5×10^6; 6) 3×10^6. The arrows identify the position of the additional maximum due to the interference of sublevels with $|\Delta M''| = 4$.

Figures 5 and 6 show the results of calculations of the $P(\omega)$ curves carried out using the wide line approximation. The curves in Figs. 5 and 6 are calculated for Q-type transitions using the parameters $\Gamma_{p0}/\Gamma_a = {}^{100}/_3$, i.e., for very strong pumping when the amplitude of a beat resonance can be very large. In Fig. 5 it was assumed that the magnetic splitting of the excited state can be ignored, i.e., that $\omega_b = 0$ in Eq. (6) and that $\omega_a = 3\times10^6$–10^8 sec^{-1}. Then, the beat resonance signals have a minimum near $\omega/\omega_a = 2$ which corresponds to partial recovery of the alignment of the ensemble. A reduction of ω_a results in a shift of the minimum to the left because the ratio $\omega_{\min}/\Gamma_a$ becomes smaller. Moreover, a small maximum appears near $\omega/\omega_a = 4$ and this clearly corresponds to recovery of the hexadecapole moment of the ensemble at the level a (Refs. 6 and 15). It should be pointed out that at $\omega_a = 10^8$ sec^{-1} we have $P = 0.5$ outside the beat resonance signal in spite of the effective optical alignment of the lower state which should reduce P (Ref. 5). The value $P = 0.5$ obtained in the range $\omega_a \gg \Gamma_a$ is associated with the Hanle effect of the ground state,[8] which recovers the degree of polarization to 0.5 in the case of weak excitation $\Gamma_{p0}/\Gamma_a \to 0$ (Fig. 1c).

It is assumed in Fig. 6 that the frequency of the splitting of the upper level was $\omega_b = 10^8$ sec^{-1} and the frequency of the splitting of the lower level ranges from $\omega_a = 10^7$ sec^{-1} to $\omega_a = 10^9$ sec^{-1}. A reduction in ω_a also reduces $\omega_{\min}/\Gamma_a$ and increases the influence of the magnetism of the excited state b, which because of the Hanle effect of the state b shifts the position of the minimum toward higher frequencies. Such a shift is discussed in Refs. 4, 6, and 19, but it is allowed there with a larger error because of the inaccuracy of the approximation adopted in the calculations, whereas the shift to the left (Fig. 5) may not appear at all. The low absolute values of P, compared with Fig. 5, are due to the depolarization because of the Hanle effect affecting the excited state b.

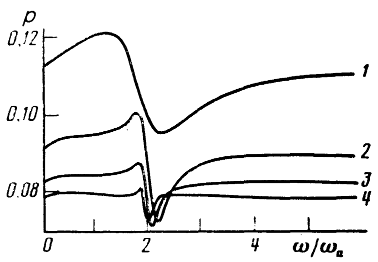

FIG. 6. Resonance beat signals calculated in the wide line approximation for $\varepsilon = 0.8$, $\omega_b = 10^8$ sec^{-1}, $\Gamma_a = 3\times10^5$ sec^{-1}, $\Gamma_{p0}/\Gamma_a = 100/3$ and different values of ω_a (sec^{-1}): 1) 10^7; 2) 3×10^7; 3) 10^8; 4) 10^9.

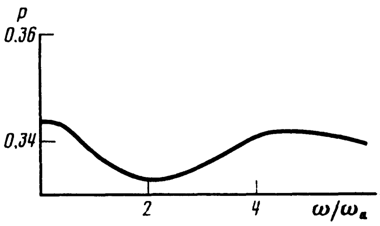

FIG. 7. Beat resonance signal calculated in the wide line approximation illustrating the appearance of an additional maximum near $\omega/\omega_a = 4$.

In contrast to Fig. 5, the results in Fig. 6 show no maximum near $\omega/\omega_a = 4$. However, if we select the parameters corresponding to the experimental results reported for K_2 in Ref. 6, namely $\omega_a = 0.675\times10^6$ sec^{-1} and $\omega_b = 10.88\times10^6$ sec^{-1} (corresponding to a field $B = 0.67$ T), and $\Gamma_{p0} = 4.5\times10^6$ sec^{-1}, an additional maximum once again appears (Fig. 7). This was the maximum observed experimentally in Ref. 6. It is interesting to note that under the conditions of Figs. 7 and 2a the shifts in Figs. 5 and 6 largely compensate each other. It should be pointed out that resonances at higher frequencies are not predicted by the calculations.

The structure of the curves for the P and R transitions in the presence of linearly polarized excitation was basically similar to the curves for the Q transitions (Figs. 5–7), but we were unable to find parameters that would reveal clearly the resonance at $\omega/\omega_a = 4$. In the case of excitation with circularly polarized light and recording of the circularly polarized components for transitions of the P and R types, we can observe two resonances: near the frequencies $\omega/\omega_a = 1$ and $\omega/\omega_a = 2$, corresponding to a partial recovery of the orientation and alignment of the lower level. The resonance beat signals also exhibit nonlinear shifts. A nonlinear shift of a beat resonance was observed experimentally[4] in the case of circularly polarized radiation.

If the nonlinear beat resonance phenomenon is used to determine the magnetic moment of a level, it is convenient to operate at higher "Q factors" $\omega_{\min}/\Gamma_a$, when the position of a resonance can be used to determine the Landé factor directly. However, there are two fundamental difficulties: firstly, the ground states of dimers are usually diamagnetic so that magnetic fields needed for a high-Q resonance may be difficult to achieve in practice. Secondly, at such high values of the magnetic field we cannot ignore the magnetism of the upper state b because of which the degree of polarization or "circularity" decreases as a result of magnetic depolarization of the fluorescence (Hanle effect), i.e., the signal amplitude decreases (Figs. 5 and 6).

In practice, we therefore have to deal with low values of the Q factor. It follows that we can determine more accurately the magnetic moment if we approximate the whole experimental dependence by a theoretical curve, as was done in the present study.

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