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# Separation of quadratic and linear external field effects in high $J$ quantum beats

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We discuss quantum beats in electronically excited molecular states with high rotational angular momenta  $J$  appearing in time resolved fluorescence in conditions of quadratic and linear energy shift dependence on magnetic quantum number  $M$  and external field strength. Density matrix formalism is used to obtain in explicit form the expressions for time dependent fluorescence intensity after  $\delta$ -function pulsed excitation. In case of pure quadratic Stark effect, which is typical for  $^1\Sigma$  state diatomics, excited state quantum beats for  $J \gg 1$  exhibit a regular, or "grill" structure, consisting of narrow equidistant "principal" peaks with equal relative amplitudes on the exponential decay background. At linear polarized excitation the time intervals between the adjacent peaks are  $2\pi/\omega_{20}$ ,  $\omega_{20}$  being the splitting frequency between coherently excited  $M$ -sublevels with  $M=2$  and  $M'=0$ . If an admixture of linear contribution is present in field induced level shifts, the grill structure is superimposed by a single frequency harmonic modulation. A special geometry was found in which the quadratic beats are fully absent and the modulated grill pattern is brought into existence only by the influence of linear term. Such a case takes place when the light polarization vector in fluorescence is directed at  $45^\circ$  angle with respect to the exciting light polarization vector and yields the most sensitive way to separate quadratic and linear contribution. We considered the examples when the first order term appears by a combined action of electric and magnetic field, as well as due to the  $e-f$  level electric field induced mixing, with the parameters typical for the NaK molecule.

## I. INTRODUCTION

Laser quantum beat spectroscopy of molecules is based on the creation of a coherent superposition of energy eigenstates by a short laser pulse. During the emission process, the time resolved intensity is modulated at frequencies corresponding to energy differences of coherently excited states. The method is essentially Doppler-free and supplies the possibility to study directly the dynamics of an excited molecular state. To have an insight into the contemporary stage of quantum beat spectroscopy of molecules one may recommend the overviews<sup>1-4</sup> and references therein. In particular, Stark induced quantum beat spectroscopy yields the most precise values of excited state electric dipole moments, which are a very sensitive measure of the electronic charge distribution in a molecular state while the magnetic, or Zeeman quantum beats yield Landé factor values.

Let us address quantum beats between magnetic sublevels ( $M$ ) of a definite rotational ( $J$ ) level which are split by an external magnetic or/and electric field. In the case of linear Zeeman effect, an isolated state with angular momentum  $J$  is split into  $2J+1$  equidistant  $M$ -sublevels due to magnetic interaction with external magnetic field  $H$  leading to energy shift

$$E_{\text{mag}}(M) = -g_J \mu_B H M, \quad (1)$$

pointing to the linear Zeeman energy  $H$ - and  $M$ -dependence. It is thus easy to achieve single frequency modulated fluorescence using, say, excitation by linear polarized light with

**E1 H.** At this geometry only the magnetic sublevels  $M, M'$ , with  $|M - M'| = 2$ , will be excited coherently and all corresponding splitting frequencies

$$\omega_{MM'} = \frac{E_{\text{mag}}(M) - E_{\text{mag}}(M')}{\hbar} = \frac{2g_J \mu_B H}{\hbar} \quad (2)$$

will coincide, being twice the Larmor frequency. From the Zeeman quantum beat signal the excited state Landé factor  $g_J$  value can be obtained.

The quantum beats induced by an external electric field (Stark quantum beats) possess, as a rule, a principal difference from the Zeeman quantum beats. Indeed, the Stark effect of a well resolved state with a definite parity ( $e$  or  $f$ ) is of second order, that is, quadratic in the external electric field strength  $\mathcal{E}$ . The energy shift  $E_{\text{el}}$  of a state  $|JM\rangle$  must be determined from perturbation theory using the perturbation Hamiltonian in the form

$$\mathcal{H}_{\text{el}} = -\mathbf{d}\mathcal{E}, \quad (3)$$

$\mathbf{d}$  being the permanent electric dipole moment. This leads to a well known<sup>2,5-7</sup> expression

$$E_{\text{el}}(J, M) = \sum_i [A_i(J) + B_i(J)M^2] d_i^2 \mathcal{E}_i^2, \quad (4)$$

where  $d_i$  is the  $\mathbf{d}$  projection on the  $i$ th principal axis of the molecule, while the coefficients  $A_i$  and  $B_i$  depend on molecular parameters, such as the rotational constant  $B_v$ . In contrast to the Zeeman effect, the energy shift in an electric field depends on  $M^2$ . Heteronuclear diatomic (or linear) molecules in  $^1\Sigma$  states, having only one permanent dipole mo-

ment component (**d**) along their internuclear axis, are the simplest examples of a pure quadratic Stark effect. For a  $^1\Sigma$  state we have

$$B(J) = \frac{1}{B_v} \frac{3}{2J'(J'+1)(2J'-1)(2J'+3)}. \quad (5)$$

This case was exploited for a number of diatomic molecules such as LiH and LiD,<sup>8,9</sup> NaH,<sup>10</sup> BaO,<sup>11</sup> and MgO (Ref. 12) in order to obtain **d** values in quantum beat experiments. The electric field induced splitting frequencies  $\omega_{MM'}$  between coherently excited  $M$ -sublevels and, hence, the quantum beat frequencies turn out to be dependent not only on the difference  $|M-M'|$  but also on the absolute values of magnetic quantum numbers  $M$  and  $M'$ . Therefore in the case of large angular momentum  $J'$  the beat signal becomes complicated, being a superposition of large number of contributions with different beat frequencies. In addition, the Stark energy  $E_{el}$  decreases rapidly with growing  $J'$  values, cf. Eqs. (4) and (5). Owing to that, observation of beats has been usually restricted in practice to small  $J'$  values, using most often excitation of  $J'=1$  or  $J'=2$  states.<sup>8-12</sup> At the same time, it is of interest to measure the  $J$ -dependence of the dipole moment.<sup>7</sup>

More generally, however, the additional external field induced energy shift can be a mixture of linear and quadratic terms. In a number of situations it is important to consider the terms proportional to  $M^2H^2$  in the mainly linear magnetic energy  $E_{mag}$ , or proportional to  $M\mathcal{E}$  in the mainly quadratic electric energy expression  $E_{el}$ . Thus, in the case when a "broad line" laser pulse excites simultaneously both  $e$  and  $f$  components due to field-induced parity mixing, matrix elements diagonal in  $J, M$  of perturbation operator  $\mathcal{H}_{el}$ , see Eq. (3) appear, thus giving rise to the linear Stark effect. This becomes true when one has  $|V_M|^2 \gg \Delta^2/4$ ,  $V_M$  being the Stark induced  $e$ - $f$  coupling matrix element, and  $\Delta$  is the energy separation between the unperturbed opposite parity  $e, f$  levels.<sup>6,13</sup> In the case of the Zeeman effect, the energies  $E_{mag}$  may possess a term quadratic in  $H$  due to intramolecular interactions of various origins,<sup>6,14</sup> such as for instance, a magnetic field induced state mixing. In a number of cases the separation of different order contributions allows recognition of perturbations of various origins. The most sensitive method to separate the roles of first and second order terms is based on recording the effects caused exclusively by symmetry changes in the angular momentum distribution of the molecular ensemble. As was demonstrated in Refs. 15,16, the effect of a small second-order contribution in a mainly linear Zeeman effect can be extracted by measuring the appearance of fluorescence polarization circularity under linear polarized excitation, yielding valuable information about the intramolecular interaction parameters.

In the present paper we are analyzing the possibility to extract the relatively small linear admixture to the mainly quadratic electric field induced energy shift from the structure of quantum beats in the time domain. We shall consider the case when the first order term is caused by the presence of a magnetic field, as well as by electric field induced  $e, f$  state mixing. This goal can be achieved in a most sensitive way by using a special geometry for quantum beat observa-

tion. We shall pay attention to states with large rotational angular momentum, when the second order term results in equidistant peaks in the time resolved fluorescence signal.

## II. GENERAL EXPRESSION FOR TIME RESOLVED FLUORESCENCE

### A. Kinetic equations for density matrix

Let us assume that the broad line pulsed optical excitation had prepared the excited state density matrix  $f_{MM'}$ ,<sup>17,18</sup> supposing the initial (ground) state density matrix  $\varphi_{\mu\mu'}$  to be diagonal over magnetic quantum numbers  $M''=\mu$ ; for simplicity  $\varphi_{\mu\mu}=1$  will be taken below. The kinetic equation can be then written in a comparatively simple form,<sup>18</sup>

$$\begin{aligned} \dot{f}_{MM'} = & \tilde{\Gamma}_p \sum_{\mu} \langle M | \hat{\mathbf{E}}^* \mathbf{D} | \mu \rangle \langle M' | \hat{\mathbf{E}} \mathbf{D} | \mu \rangle^* \\ & - (\Gamma + i\omega_{MM'}) f_{MM'}, \end{aligned} \quad (6)$$

where

$$\tilde{\Gamma}_p = \tilde{G} \delta(0) \quad (7)$$

is the reduced absorption rate for a  $\delta$ -function pulse,  $\Gamma$  is the total excited state relaxation rate,  $\hat{\mathbf{E}}$  is the light polarization unit vector of the exciting light beam,  $\mathbf{D}$  is the transition dipole moment, and  $\omega_{MM'}$  is the level splitting frequency caused by the static external field effect, cf. Eq. (2). It is easy to find the time evolution  $f_{MM'}(t)$  as

$$f_{MM'}(t) = f_{MM'}(0) e^{-(\Gamma + i\omega_{MM'})t}. \quad (8)$$

The next task is to calculate the matrix elements  $f_{MM'}(0)$ . Using Wigner-Eckart theorem,<sup>19</sup> we get

$$\begin{aligned} \langle M | \hat{\mathbf{E}}^* \mathbf{D} | \mu \rangle &= \sum_q (E^q)^* \langle M | D^q | \mu \rangle \\ &= \frac{1}{\sqrt{2J'+1}} \sum_q (E^q)^* C_{J''\mu 1 q}^{J' M} (J' \| D \| J''), \end{aligned} \quad (9)$$

where  $E^q$  and  $D^q$ ,  $q=0, \pm 1$  are cyclic components of  $\hat{\mathbf{E}}$  and  $\mathbf{D}$ ,  $C_{a\beta\gamma}^{\alpha}$  are Clebsch-Gordan coefficients, and  $(J' \| D \| J'')$  are reduced matrix elements of the electric dipole transition moment. After solving Eq. (6) with  $\delta$ -function pulse excitation and accounting for Eq. (9), we arrive at

$$\begin{aligned} f_{MM'}(0) &= \tilde{G} \sum_{\mu} \langle M | \hat{\mathbf{E}}^* \mathbf{D} | \mu \rangle \langle M' | \hat{\mathbf{E}} \mathbf{D} | \mu \rangle^* \\ &= \tilde{G} \frac{|(J' \| D \| J'')|^2}{2J'+1} \sum_{\mu q_1 q_2} (E^{q_1})^* E^{q_2} C_{J''\mu 1 q_1}^{J' M} \\ &\quad \times C_{J''\mu 1 q_2}^{J' M'}. \end{aligned} \quad (10)$$

This allows us to derive the time evolution  $f_{MM'}(t)$  for arbitrary excited light polarization, which is determined by the cyclic components  $E^q$ , which are related to the cartesian components of the vector  $\mathbf{E}$  as

$$E^{+1} = -\frac{1}{\sqrt{2}}(E_x - iE_y) = -\frac{1}{\sqrt{2}}E \sin \theta e^{-i\varphi},$$

$$E^0 = E_z = E \cos \theta, \quad (11)$$

$$E^{-1} = \frac{1}{\sqrt{2}}(E_x + iE_y) = \frac{1}{\sqrt{2}}E \sin \theta e^{i\varphi},$$

where  $\theta$  and  $\varphi$  are the spherical angles defining  $\mathbf{E}$  vector orientation in space.

Let us consider the case of linear polarized excitation,  $\mathbf{E}$  being orthogonal to the external field direction, or to the  $z$  axis of quantization. Supposing that  $\theta = \varphi = \pi/2$  and taking  $|\mathbf{E}|=1$ , we get from Eq. (11),

$$E^{\pm 1} = \frac{i}{\sqrt{2}}, \quad (12)$$

$$E^0 = 0.$$

By putting Eq. (12) into Eq. (10) and then into Eq. (8), after summation over  $\mu$ ,  $q_1$  and  $q_2$ , we finally obtain the time evolution of the nonvanishing density matrix elements in the form

$$f_{MM}(t) = \frac{G}{2} [(C_{J''M-111}^{J'M})^2 + (C_{J''M+11-1}^{J'M})^2] e^{-\Gamma t}, \quad (13)$$

$$f_{M-1M+1}(t) = \frac{G}{2} C_{J''M-1-1}^{J'M-1} C_{J''M11}^{J'M+1} e^{-(\Gamma + i\omega_{M-1M+1})t}, \quad (14)$$

$$f_{M+1M-1}(t) = \frac{G}{2} C_{J''M1-1}^{J'M-1} C_{J''M11}^{J'M+1} e^{-(\Gamma + i\omega_{M+1M-1})t}, \quad (15)$$

where  $G = \tilde{G} | \langle J' \| D \| J'' \rangle |^2 / (2J' + 1)$  is the dynamic part of the absorption probability, whilst the Clebsch–Gordan coefficients characterize the angular dependence of light absorption (“geometric” factor). Expressions (14) and (15) demonstrate clearly that for linearly polarized excitation with  $\mathbf{E} \perp \mathbf{z}$ , simultaneous transitions take place from the ground state sublevel  $\mu = M$  to the excited state  $M+1$  and  $M-1$  magnetic sublevels, thus introducing a coherence between  $M+1$  and  $M-1$  states, which is characterized by the nondiagonal density matrix elements  $f_{M-1M+1}$ ,  $f_{M+1M-1}$ , and results in quantum beats at the corresponding frequencies.

## B. Fluorescence intensity in the time domain

The density matrix elements  $f_{MM'}$  allow calculation of the fluorescence signal. If the light is emitted in a  $J' \rightarrow J''_1$  transition, the fluorescence intensity with a definite polarization  $\mathbf{E}_1$  can be found as<sup>17,18</sup>

$$I_f(\hat{\mathbf{E}}_1) = \tilde{I}_0 \sum_{MM'\mu} \langle M | \hat{\mathbf{E}}_1^* \mathbf{D} | \mu \rangle \langle M' | \hat{\mathbf{E}}_1 \mathbf{D} | \mu \rangle^* f_{MM'}$$

$$\propto \frac{1}{2J'+1} \sum_{MM'} A_{MM'} f_{MM'}, \quad (16)$$

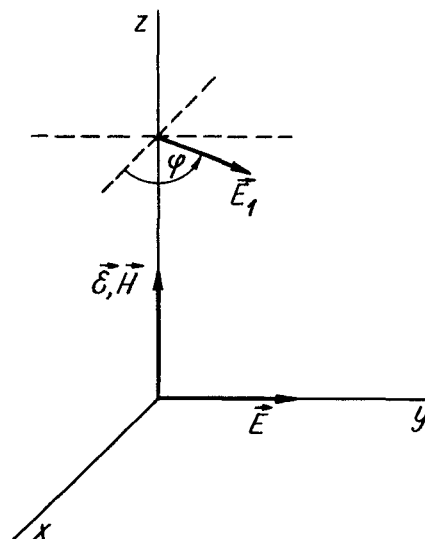


FIG. 1. Geometry of excitation and observation of fluorescence,  $\mathbf{E}$  and  $\mathbf{E}_1$  are polarization vectors for excitation and observation of fluorescence.

where matrix elements  $A_{M,M}$  form the so-called “observation matrix.” For the observation geometry shown in Fig. 1, the  $E_1^q$  components are

$$E_1^{\pm 1} = \mp \frac{1}{\sqrt{2}} e^{\mp i\varphi}, \quad E_1^0 = 0. \quad (17)$$

Applying Wigner–Eckart theorem (9), after summation over  $\mu$ ,  $q_1$ , and  $q_2$ , one can obtain the nonvanishing  $A_{M,M}$  elements as

$$A_{MM} = \frac{1}{2} [(C_{J''M-111}^{J'M})^2 + (C_{J''M+11-1}^{J'M})^2],$$

$$A_{M-1M+1} = -\frac{1}{2} e^{2i\varphi} C_{J''M11}^{J'M+1} C_{J''M-1-1}^{J'M-1}, \quad (18)$$

$$A_{M+1M-1} = -\frac{1}{2} e^{-2i\varphi} C_{J''M11}^{J'M+1} C_{J''M1-1}^{J'M-1}.$$

Putting Eqs. (13)–(15) and (18) into Eq. (16), we arrive at a time dependent intensity expression in explicit form

$$I_f(t) \propto \frac{1}{4} \frac{1}{2J'+1} e^{-\Gamma t} \sum_M \{ [(C_{J''M-111}^{J'M})^2 + (C_{J''M+11-1}^{J'M})^2] [(C_{J''M-111}^{J'M})^2 + (C_{J''M+11-1}^{J'M})^2] - 2 \cos(\omega_{M+1M-1}t - 2\varphi) \times C_{J''M-1-1}^{J'M-1} C_{J''M11}^{J'M+1} C_{J''M1-1}^{J'M-1} C_{J''M11}^{J'M+1} \}. \quad (19)$$

As may be seen, the exponential decay of fluorescence intensity is harmonically modulated at frequencies  $\omega_{M+1M-1}$ .

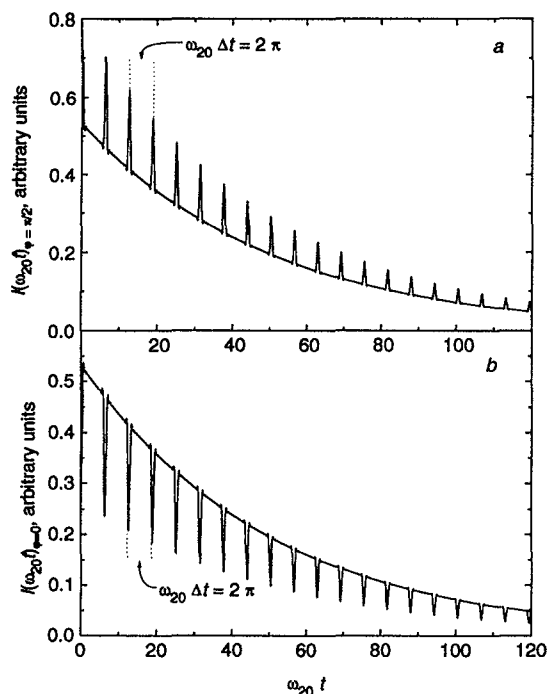


FIG. 2. Numerical simulation of quadratic Stark effect induced "grill" quantum beat structure in fluorescence from  $J' = 10$ . (a) Parallel direction of excitation ( $\mathbf{E}$ ) and observation ( $\mathbf{E}_1$ ) vectors, when  $\varphi = \pi/2$  in Fig. 1. (b) Orthogonal direction of  $\mathbf{E}$  and  $\mathbf{E}_1$ , when  $\varphi = 0$  in Fig. 1.

### III. SPECIFIC QUANTUM BEAT MANIFESTATIONS IN EXCITED STATES WITH $J \gg 1$

#### A. Pure quadratic Stark quantum beats

An impressive amount of experimental results with the aim to determine molecular electric dipole moments has been obtained by the second-order Stark quantum beats method for the  $^1\Sigma$ -type excited states, cf. Refs. 7–12. The obtained data and the description of the beat signal are restricted however to small  $J'$  values ( $J' = 1$  or 2 typically). Let us examine the beat signal given by Eq. (19) at  $J \gg 1$ . In the simplest case of Stark induced energy shifts given by Eqs. (4) and (5), one gets

$$\omega_{M+1M-1} = 12MB(J) = M\omega_{20}. \quad (20)$$

Hence, as it is easy to see, all frequencies  $\omega_{MM'}$  entering Eq. (19) will be integer multiples of the frequency  $\omega_{20}$ , which corresponds to the splitting between the magnetic sublevels  $M = 2$  and  $M' = 0$  and serves as the "fundamental" beat frequency. To observe the beats during the fluorescence decay time, one has therefore to apply a static electric field of sufficient strength to  $\omega_{20}/\Gamma \geq 1$ .

A concrete example of such beat signal manifestation is given in Fig. 2 for a  $Q \uparrow Q \downarrow$ -type molecular transition with  $J'' = J' = J_1'' = 10$ . Figure 2(a) demonstrates the case when linear polarization vectors in excitation ( $\mathbf{E}$ ) and observation ( $\mathbf{E}_1$ ) are parallel to each other, that is when  $\varphi = \pi/2$  in Fig. 1. The signal in Fig. 2(b) corresponds to orthogonally polarized excitation and observation vectors, when  $\varphi = 0$  in Fig. 1. The beat signal consists of equidistant "principal" peaks, the

sharpness of which becomes more pronounced with growing  $J'$ . Such a structure follows from analysis of the conditions of constructive interference in the fluorescence signal, cf. Eq. (16), of the density matrix elements  $f_{MM'}$  given by Eqs. (14), (15) for linear dependence of  $\omega_{M-1M+1}$  on  $M$ , cf. Eq. (20). Indeed, for  $M = 1, 2, \dots$  we have  $\omega_{20} = 12B(J)$ ,  $\omega_{31} = 24B(J)$ ,  $\dots$ . This means that the phases of all matrix elements  $f_{M+1M-1}$ ,  $f_{M-1M+1}$  are again in coincidence after the time interval  $\Delta t = 2\pi/\omega_{20}$ . As follows from the second term in Eq. (19), this provides the constructive contribution of all  $f_{M+1M-1}$  and  $f_{M-1M+1}$  in the fluorescence intensity  $I_f(t)$ .

It is interesting to note that such "Stark grill" structure resembles the light diffraction pattern produced by a diffraction grating in optics. In the case of diffraction grating with  $N$  slits, between each two adjacent "principal maxima" we have  $N-2$  small secondary maxima, separated by  $N-1$  points of zero intensity. Similarly, in the case of pure quadratic Stark quantum beats from a level  $J'$ , between each two adjacent "principal peaks" we have  $J'-2$  small secondary peaks (practically indistinguishable in the scale of Fig. 2), separated by  $J'-1$  points of zero deflection from exponential decay. In both cases the intensity of the secondary peaks decreases rapidly as  $N$  or  $J'$  increase while the principal maxima are becoming sharper. It is interesting that the similar "Stark grill" structure has been predicted in Ref. 20 for nonoptical Stark induced orientation of previously aligned ground  $^1\Sigma$  state beam molecules, which are moving with velocity  $\mathbf{v}$ , passing through an  $\mathcal{E}$  field region of length  $L$ , the angle between  $\mathcal{E}$  and  $\mathbf{v}$  being  $\pi/4$ .

To give an idea of "grill" Stark beat manifestation in a specific molecule, we have chosen in Fig. 2 the parameters typical for the NaK molecule in its  $(3)^1\Sigma^+$  state,<sup>21,22</sup> namely  $B_v = 0.059 \text{ cm}^{-1}$ ,  $d = 2 \text{ D}$ ,  $\Gamma = 8.97 \times 10^7 \text{ s}^{-1}$ . According to Eqs. (4) and (5), this leads to  $\omega_{20} = 4.488 \times 10^9 \text{ s}^{-1}$  for  $J' = 10$  at electric field strength  $\mathcal{E} = 100 \text{ kV/cm}$ , when the "grill" structure is well developed during the lifetime of the excited state after pulsed excitation at  $t = 0$ . The "grill" signals seem to be a source of obtaining precise permanent electric dipole moment values and/or rotational constant values ( $B_v$ ) for high  $J'$  excited states. It should be stressed that, from another point of view, such a structure is an indication that the energy shifts are produced by a pure quadratic Stark effect, because even a small deviation of  $E_{el}(J, M)$  from Eq. (4) will, as will be shown below, drastically change the beat pattern.

#### B. Separation of linear and quadratic contributions

Let us now assume that the additional energy shift caused by an external field contains a linear term with respect to  $M$ , which is an admixture into the mainly quadratic dependence of energy shifts on  $M$  values. The most obvious example is simultaneous Stark–Zeeman quantum beats. Such beats for the states with low  $J'$  values were observed by Brucat and Zare<sup>23</sup> on  $\text{NO}_2$  molecules in combined electric and magnetic fields.

Let us suppose that both static electric and magnetic field vectors are directed along the  $z$ -axis, cf. Fig. 1. Figure 3 demonstrates the expected changes in the beat signal which

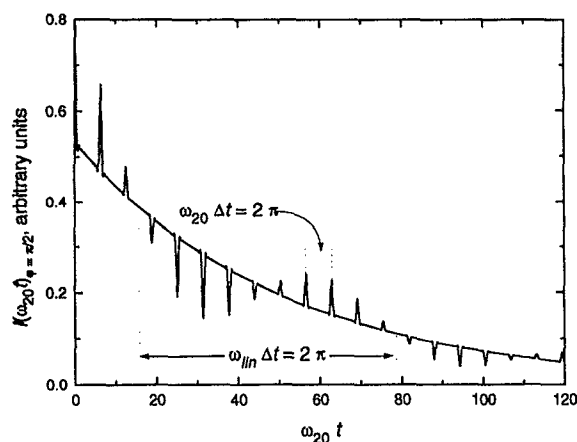


FIG. 3. Changes in beat structure shown in Fig. 2(a) when external magnetic field  $\mathbf{H} \parallel \mathcal{E}$  is applied, producing a linear magnetic splitting,  $\omega_{\text{lin}} = 2g_J \mu_B H / \hbar = 0.1 \omega_{20}$ .

has been shown in Fig. 2. In addition to the Stark energy level splitting  $\omega_{M+1M-1}$ , assume that the magnetic field produces a level splitting between  $M+1$  and  $M-1$  states equal to  $\omega_{\text{lin}} = 0.1 \omega_{20}$ , which is  $M$ -independent, cf. Eq. (2). Figure 3 demonstrates that the “grill” structure becomes harmonically modulated by a single frequency  $\omega_{\text{lin}}$ .

The signal possesses more interesting features when fluorescence is observed which is linearly polarized at angle  $\varphi = \pi/4$  (cf. Fig. 1). For this geometry, the pure quadratic beats are absent, as may be seen from Fig. 4(a), the only difference of which from the curves in Fig. 2 is that  $\varphi$  is equal to  $\pi/4$ . The situation changes drastically under the in-

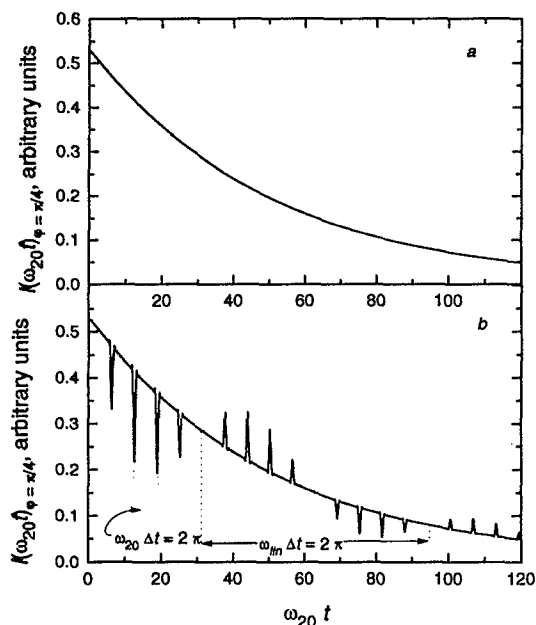


FIG. 4. Fluorescence decay observed at the angle  $\widehat{\mathbf{E}, \mathbf{E}_1} = \pi/4$  between the excitation ( $\mathbf{E}$ ) and observation ( $\mathbf{E}_1$ ) vectors. (a) “Pure” quadratic Stark effect, as in Fig. 2. (b) An additional magnetic field is applied, as in Fig. 3.

fluence of a linear contribution to the level splittings, when both Stark and Zeeman beats are again pronounced and well separable, see Fig. 4(b).

It ought to be noted that it is a manifestation of the linear  $M$ -level tuning which brings back into existence the “grill” structure caused by quadratic Stark effect. In other words, in this geometry the appearance of the peaks in the fluorescence decay is caused exclusively by the presence of the linear energy term, thus being a very sensitive test of the presence of the latter.

It seems interesting to suggest a pictorial explanation of the situation depicted in Fig. 4. For this purpose let us turn to a vector model. Excitation by pulsed linearly polarized light creates an anisotropic spatial distribution of excited state angular momenta  $\mathbf{J}'$ .<sup>19,24</sup> This distribution possesses cylindrical symmetry with respect to the  $\mathbf{E}$ -vector, being symmetrical with respect to reflection in the plane which is orthogonal to the  $\mathbf{E}$  direction. The magnetic field  $\mathbf{H}$  causes all momenta  $\mathbf{J}'$  of the molecular ensemble to precess around the  $\mathbf{z}$ -axis. As follows from Eq. (1), all angular momenta  $\mathbf{J}'$ , with any  $M$  value (which now define the angle between  $\mathbf{J}'$  and  $\mathbf{z}$ ), will precess around  $\mathbf{H}$  with the same angular velocity. The whole “rosette of  $\mathbf{J}'$ -vectors” will therefore precess as a single entity, maintaining its shape! It is clear that such a precession leads to harmonic modulation of the exponential decay at twice the Larmor frequency, when fluorescence is viewed, say, in the  $\mathbf{z}$ -direction through a linear polarizer which defines the  $\mathbf{E}_1$ -vector, cf. Fig. 1, at any  $\varphi$  value. This is a well known<sup>25</sup> “classical” interpretation of pure magnetic (Zeeman) quantum beats.

The situation is essentially different in case of the second order Stark effect. As follows from electric field energy level expressions (4) and (5), the angular momenta  $\mathbf{J}$  possessing different  $M$  values will now, after time interval  $t$ , rotate around  $\mathbf{z}$  through different angles. Moreover, the direction of rotation for two angular momentum spatial orientations determined by  $+M$  and  $-M$  will be opposite. The beat frequencies will therefore be dependent on  $\mathbf{J}'$  spatial orientation. A rephasing effect must occur after a definite time interval, when the initial  $\mathbf{J}'$  distribution is again restored, producing peaks in fluorescence, cf. Fig. 2. There exists, however, a special angle between  $\mathbf{E}$  and  $\mathbf{E}_1$ , cf. Fig. 1, which is equal to  $\pi/4$ , when the special rotation will not produce any detectable change in emitted light intensity, as in Fig. 4(a). An intuitive explanation of this fact is as follows. At  $\varphi = \pi/4$  the rotation around  $\mathcal{E} \parallel \mathbf{z}$  of the half of  $\mathbf{J}'$ 's, say, with  $M > 0$ , will lead to an increase of fluorescence, whilst the other half, with  $M < 0$ , due to a rotation in the opposite sense, will lead to a decrease of the fluorescence by the same amount. Of course, such cancellation follows also from a formal analysis of the influence on the fluorescence intensity of the second term in Eq. (19), in which the even function  $\cos(\omega_{M+1M-1}t - 2\varphi)$  can be replaced at  $\varphi = \pi/4$  by the odd function  $-\sin(\omega_{M+1M-1}t)$ , and, as a result the terms with  $\pm M$ , in the summation over  $M$  will cancel each other in the case of a pure quadratic Stark effect. If now an additional external magnetic field  $\mathbf{H}$  is applied in the  $\mathcal{E} \parallel \mathbf{z}$  direction, the symmetry of  $\mathbf{J}'$ 's with respect to the  $\mathbf{E}$ -vector is broken due to even a slight precession of the before  $\mathbf{J}$  distribution about  $\mathbf{H}$ ,

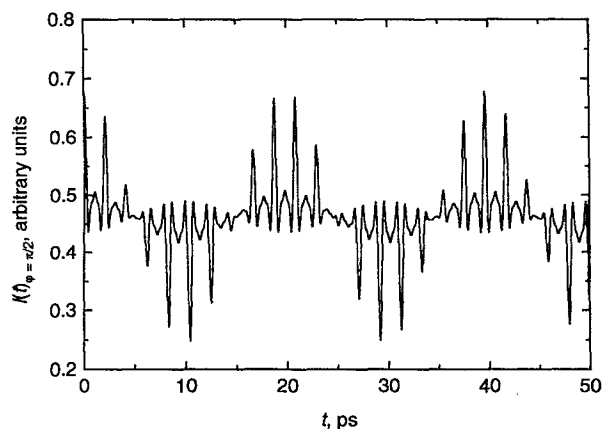


FIG. 5. Numeric simulation of quantum beat signal for a  ${}^1\Pi$  state with combined first and second order Stark effects, for  $J'=5$ ,  $\mathcal{E}=100$  kV/cm.

thus restoring immediately the simultaneous manifestations of both second order Stark and first order Zeeman quantum beats in fluorescence with  $\varphi=\pi/4$ , cf. Fig. 4(b).

Now let us consider the case when the linear term appears as a result of a Stark effect in a state with  $\Lambda \neq 0$  due to electric field induced  $e-f$  mixing. An optical  ${}^1\Sigma-{}^1\Pi$  transition produces molecules in either  $e$  or  $f$  states, which are now coupled by the Stark interaction. The theory of Stark spectroscopy in a  ${}^1\Pi$  state is given in Ref. 13, while the experiments with the  $B\,{}^1\Pi$  state of NaK molecule has been carried out in Ref. 26. In that case the Stark energy of the  $e-f$  complex takes the form

$$E_{\text{el}} = E_{\text{el}}^{\text{rot}}(J, M) \pm \frac{1}{2} \sqrt{[qJ'(J'+1)]^2 + 4 \left[ \frac{d\mathcal{E}M}{J'(J'+1)} \right]^2}, \quad (21)$$

where  $E_{\text{el}}^{\text{rot}}(J, M)$  is the so-called rotational term defined by Eq. (4) and plus or minus signs correspond to  $e$  or  $f$  components. It is easy to imagine that at high electric field strength, when the term  $\Delta = qJ'(J'+1)$  in Eq. (21), which reflects the  $\Lambda$ -doubling, may be negligible, the conditions are met for linear with respect to  $M$  and  $\mathcal{E}$  an electric energy expression, and

$$E_{\text{el}} \approx E_{\text{el}}^{\text{rot}}(J, M) \pm \frac{d\mathcal{E}M}{J'(J'+1)}. \quad (22)$$

For large  $\mathcal{E}$  and not very large  $J'$  values the quadratic term may dominate in expression (21), and we again may expect the exhibition of a “grill” structure, which is modulated by a single harmonic frequency. A specific example for such a case in a  $Q\uparrow Q\downarrow$  transition at  $J'=5$  is shown in Fig. 5, where the parameters correspond to the NaK molecule in the  $D\,{}^1\Pi$  state, namely  $d=7.5$  D,<sup>22</sup>  $\tau \approx 20$  ns,<sup>27</sup>  $B_v=0.0677$  cm<sup>-1</sup>,<sup>28</sup> and the electric field strength is assumed to be 100 kV/cm. The signal in Fig. 5 is calculated assuming that “total”  $e-f$  mixing has taken place between all magnetic sublevels, except  $M=0$ . The fact that the  $M=0$  sublevels of  $e$  and  $f$  components are not mixed by the electric field causes the minor distortion in the beat signal, leading only to the in-

crease of the amplitudes of the secondary peaks, cf. Fig. 5. Despite these distortions, we can still clearly distinguish the two structures in the fluorescence kinetics. The fast one consists of the sharp peaks, the separation of which is determined by  $\omega_{20}$ , while the slow modulation of the intensity of those peaks is determined by the second summand in Eq. (22) being linearly dependent on  $\mathcal{E}$  and  $M$ . Of course, in the present example, due to large  $\mathcal{E}d$  product and relatively small  $J$  values, the modulated Stark grill structure shows itself at a time scale which is much smaller than the lifetime  $\tau=\Gamma^{-1}$ .

#### IV. CONCLUSIONS

We have demonstrated that a simplification of Stark quantum beat structure in the time domain may be achieved for excited molecular states with  $J' \gg 1$  in the case of “pure” quadratic  $M$ -level splitting. The Stark beat pattern then exhibits the “grill” structure consisting of equidistant narrow peaks, the separation of which yields the value of the permanent electric dipole moment. A quantitative calculation leads to the expectation that such a structure could be recorded during the typical fluorescence decay time of a few tens of nanoseconds, for  $J'$  values up to, say,  $J'=20$  or more, for an excited state with the permanent electric dipole moment of an order of 1 D, since electric field strengths of 100–300 kV/cm are now achievable. From another point, such a beat pattern may be useful for optical control of electric field strength.

The manifestation of high  $J$  state quantum beats is changed when an admixture of a linear term is present in the  $M$ -level energy dependence on external field. Namely, the peak amplitudes are now harmonically modulated with 100% depth at the single frequency of the coherently excited  $M$ -level splitting which is caused by the contribution of the linear term. This permits separation of the quadratic and linear contributions to the energy shifts. The most sensitive probe of the presence of the linear term can be achieved in a special geometry, when the quadratic beats would not be observed if the linear term were absent. Such a method is based on the breaking of the cylindrical symmetry of the angular momentum distribution of the E vector of the linear polarized excitation. We believe that the extraction of different order contributions to the external field induced energy shifts is of practical value since detailed information on the magnetic level tuning is, as a rule, not available from direct measurements.

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