

## 230. Molecular Quantum Beat Spectroscopy in External Fields as a Sensitive Probe of Excited State Properties

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### Summary

The new phenomenon of the external field dependence of quantum beats in polyatomic molecules is studied on a model which offers analytical formulas for a series expansion to lowest order in the field. A comparison with recent experiments on the magnetic field effect in biacetyl suggests that, in addition to the level shift, the triplet deactivation is also strongly field-dependent. New experiments are proposed.

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**1. Introduction.** – The high density of excited states of polyatomic molecules has people made believe for a long time that a reversible phenomenon like singlet-triplet quantum beats in the emitted luminescence intensity could not exist at all, not even under isolated molecule conditions since too many final states would contribute to an irreversible deactivation of the initially excited state. However, this can not be justified without specifying details of the preparation of the excited state. The wide range of excitation possibilities under quite extreme conditions of experimental observation shows that quantum oscillations should be expected even in polyatomic molecules [1] [2]. Indeed, the experimental situation has drastically changed with increasing accessibility of very selective and well-defined excitations as due to the new laser and molecular beam technology. As a consequence, the first intramolecular quantum beats in a polyatomic molecule could finally be discovered in an experiment on biacetyl [3] [4].

Recently, an experiment on magnetic field dependence of beats has been reported [5] [6] which is not particularly suited for a test of theoretical models [4] [6–8]. The most detailed analyses of beat experiments for methylglyoxal and biacetyl have been published last year [9–11].

Quantum beat spectroscopy allows the most direct access to internal-coupling matrix elements by largely eliminating the problems of inaccurately known density of states and *Franck-Condon* factors since, due to sharper selection rules, only a few states come into play. In an ideal beat experiment involving only two exactly or nearly degenerate levels the beat amplitude is particularly large and the beat frequency yields, to a good accuracy, directly the magnitude of the desired coupling matrix element [2] [4] modified by a vibrational overlap integral, at least as long as

an adiabatic approximation holds. For non-adiabatic conditions this point is not so clear. On the other hand, it may be assumed that rotational overlap integrals are not significant since the rotational constants for the two beating states will not differ appreciably from each other and for singlet-triplet transitions selection rules restrict the interaction to levels with identical rotational quantum numbers.

By use of external fields the above described ideal beat situation can be achieved since the relative energetic position of involved levels can be shifted arbitrarily. One may think of electric fields associated with linear and quadratic *Stark* effects, or of magnetic fields with a corresponding wide variety of molecular *Zeeman* effects [12] [13]. Mainly by microwave spectroscopy, it should be possible to get very detailed information about these molecular properties. In addition, by keeping the excitation conditions fixed, magnetic-field-dependent quantum beat spectroscopy can reveal much of the energetic structure of the triplet level manifold, as well as the energy dependence of internal coupling and deactivation parameters. It is the aim of this paper to study, in particular, the external field influence on quantum beats and their characteristic experimental parameters by extracting analytical expressions from an exactly solvable model. The emphasis will be on rather weak fields since, in many cases, they will be already sufficient to appreciably alter the observed beat pattern [5] [6].

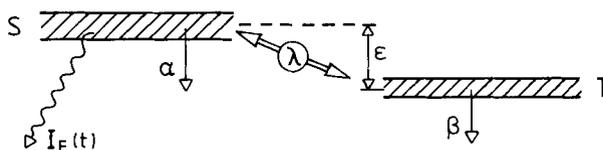


Fig. 1. Model for singlet-triplet quantum beats

In the simplest model for a singlet-triplet quantum beat description as shown in *Figure 1*  $\alpha$  denotes the irreversible deactivation of the singlet comprising radiative as well as radiationless processes whereas  $\beta$  is considered to describe dominantly radiationless processes of the triplet-level including possible collisionally induced effects. A zero-order level displacement  $\epsilon$  (valid for  $\lambda=0$ ) is introduced which, for our purposes, will be field-dependent and can, of course, take on negative as well as positive values. The effective spin-orbit interaction parameter is indicated by  $\lambda$ . Under the assumption of exact initial excitation of a singlet rovibronic state, the normalized time-dependent fluorescence intensity  $I_F(t)$  is most conveniently expressed in terms of experimentally observable quantities [2] [14] as

$$I_F(t) = A_f \exp[-k_f t] + A_s \exp[-k_s t] + A_b \exp[-k t] \sin(2\omega t + \delta) \quad (1)$$

where the index f refers to the fast, s to the slow and b to the beating component ( $k_s \leq k \leq k_f$ ). In the following, we investigate the explicit dependence of the above quantities upon external fields *via* the field dependence of the level-shift parameter  $\epsilon$ .

2. **Influence of an external field.** – The derivation of the general exact solutions for the model of *Figure 1* can be found in [2] [4]. The decay of the beating component is independent of  $\varepsilon$  and given by

$$k = \frac{1}{2} (a + \beta) \quad (2)$$

whereas all other quantities of *Equation 1* may be expressed in terms of an auxiliary function of  $\varepsilon$ ,

$$G(\varepsilon) = \{ [16\lambda^2 - (a - \beta)^2]^2 + [8(a - \beta)^2 + 128\lambda^2 + 16\varepsilon^2]\varepsilon^2 \}^{1/2} \quad (3)$$

in the following way,

$$\left. \begin{matrix} k_f(\varepsilon) \\ k_s(\varepsilon) \end{matrix} \right\} = k \pm \frac{1}{\sqrt{8}} [G(\varepsilon) - 4\varepsilon^2 + (a - \beta)^2 - 16\lambda^2]^{1/2} \quad (4)$$

where upper and lower functions on the left hand side of *Equation 4* should be associated with upper and lower sign [15] on the right hand side,

$$\left. \begin{matrix} A_f(\varepsilon) \\ A_s(\varepsilon) \end{matrix} \right\} = \frac{1}{4} \left\{ 1 + \frac{[(a - \beta)^2 + 4\varepsilon^2 \pm \sqrt{2} (a - \beta) \{G(\varepsilon) - 4\varepsilon^2 + (a - \beta)^2 - 16\lambda^2\}^{1/2} \pm \sqrt{8} \varepsilon \{G(\varepsilon) + 4\varepsilon^2 - (a - \beta)^2 + 16\lambda^2\}^{1/2}]}{G(\varepsilon)} \right\} \quad (5)$$

$$A_b(\varepsilon) = \frac{\{ [G(\varepsilon) - 4\varepsilon^2 - (a - \beta)^2]^2 + 2[(a - \beta) \{G(\varepsilon) + 4\varepsilon^2 - (a - \beta)^2 + 16\lambda^2\}^{1/2} - 2\varepsilon \{G(\varepsilon) - 4\varepsilon^2 + (a - \beta)^2 - 16\lambda^2\}^{1/2}]^2 \}^{1/2}}{2G(\varepsilon)} \quad (6)$$

$$\omega(\varepsilon) = \frac{1}{2\sqrt{8}} [G(\varepsilon) + 4\varepsilon^2 - (a - \beta)^2 + 16\lambda^2]^{1/2} \quad (7)$$

$$\delta(\varepsilon) = \arcsin \{ [1 - A_f(\varepsilon) - A_s(\varepsilon)] / A_b(\varepsilon) \} \quad (8)$$

The general behavior of amplitudes, frequency and deactivation constants as a function of  $\varepsilon$  is displayed in *Figures 2* and *3* for the particular choice of parameters:  $\alpha = 5 \times 10^6 \text{ s}^{-1}$ ,  $\beta = 0$ ,  $\lambda = 7 \times 10^6 \text{ s}^{-1}$  (these values are appropriate for biacetyl). The beat amplitude reaches its maximum and the frequency its minimum exactly on resonance ( $\varepsilon = 0$ ). The total intensity oscillates between zero and a multi-exponentially decaying maximum. With increasing modulus of  $\varepsilon$ , the beat amplitude decreases, the frequency increases and the whole beat pattern gradually goes over into a biexponential and, finally, a single exponential decay. Therefore, field-dependent measurements offer the possibility to switch between beating and non-beating decay of a pair of levels. The details depend, of course, on the particular dependence of  $\varepsilon$  on the applied field, *i.e.*, it should be possible to discriminate linear and quadratic effects or even higher order effects. An example of a magnetic field effect will be considered in *Section 3*.

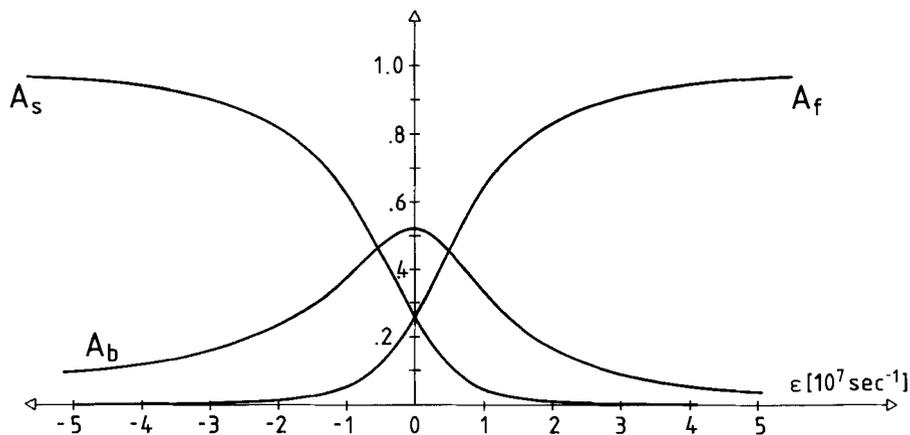


Fig. 2. Amplitudes of pure exponential and beating components of the fluorescence intensity as a function of zero-order singlet-triplet energy difference

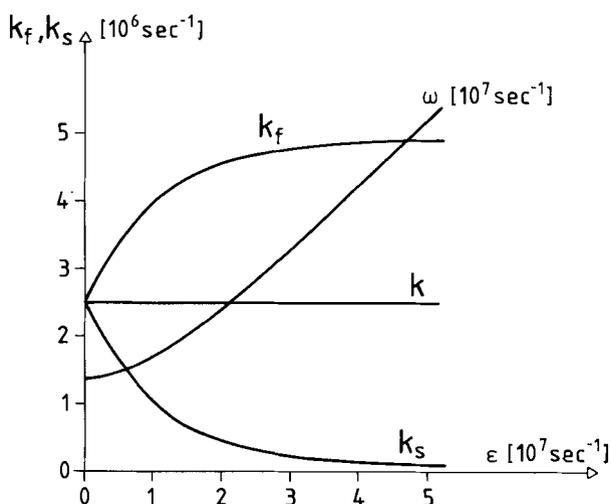


Fig. 3. Dependence of decay constants and beat frequency on zero-order singlet-triplet energy difference

In particular, a detailed study of the change of beat pattern in the vicinity of the resonance provides useful information about the basic parameters. For this case, an analytic series expansion to lowest order in  $\varepsilon$  yields *Equations 9–15*.

$$\omega(\varepsilon) \cong \frac{x}{4} + \left( \frac{32\lambda^2 + x^2}{4x^3} \right) \varepsilon^2 \quad (9)$$

$$\left. \begin{matrix} k_f(\varepsilon) \\ k_s(\varepsilon) \end{matrix} \right\} \cong k \pm \left[ \left( \frac{\alpha - \beta}{x} \right)^2 + \frac{1}{2} \right] |\varepsilon| \quad (10)$$

$$\left. \begin{array}{l} A_f(\varepsilon) \\ A_s(\varepsilon) \end{array} \right\} \cong \frac{4\lambda^2}{x^2} \pm \left\{ \frac{\alpha - \beta}{x^3} [(a - \beta)^2 + 4x^2]^{1/2} + \frac{1}{x} \right\} \varepsilon \quad (11)$$

$$A_b(\varepsilon) \cong \frac{8\lambda^2}{x^2} + b_1\varepsilon^2 + b_2|\varepsilon| \varepsilon \quad (12)$$

$$x = [16\lambda^2 - (\alpha - \beta)^2]^{1/2} \quad (13)$$

$$b_1 = \frac{31}{4\lambda^2} \left( \frac{\alpha - \beta}{x} \right)^4 + 27 \left( \frac{\alpha - \beta}{4\lambda x} \right)^2 + \frac{1}{8\lambda^2} - 1024 \frac{\lambda^4}{x^6} \quad (14)$$

$$b_2 = \frac{\alpha - \beta}{16x\lambda^2} \left[ \left( \frac{\alpha - \beta}{x} \right)^2 + \frac{1}{2} \right]^{1/2} \quad (15)$$

**3. The magnetic field effect in biacetyl.** – A first experiment on the magnetic field influence on molecular quantum beats detected in the fluorescence of biacetyl has recently been reported by *Henke et al.* [5] [6]. The main finding is a decrease of the lifetime already for extremely weak magnetic fields, *i.e.*, by about 30% from 0 to 4 Gauss, or finally, by about 65% at 40 Gauss (within experimental accuracy).

In a first attempt to interpret this effect in terms of the present model any triplet deactivation ( $\beta = 0$ ) including possible hot phosphorescence [14] is neglected to check whether the whole field variation of physical parameters can be explained purely in terms of  $\varepsilon$  (H), *i.e.*, the field-induced displacement of a triplet sublevel beating against the singlet one. Since the decay constant increases and, at the same time, the beat frequency seems to decrease with increasing field, one concludes from *Figures 2* and *3* that the starting value of  $\varepsilon$  for zero-field should be negative, *i.e.*, the accepting triplet level lies below the singlet and the dominant exponential component is the slow one, whereas the fast component is almost negligible. For detailed interpretations, much more experimental data would be necessary. Nevertheless, a rough fit to the available data is presented in *Figure 4* where also the rather strong influence of a variation of  $\beta$  is displayed. This already suggests that a disappearance of beats is due to an interplay between the field dependencies of  $\varepsilon$  and  $\beta$ . since for  $\beta = \text{const.}$  or, particularly,  $\beta = 0$ , the beat amplitude rather increases with increasing field, although the lifetime shortens. The numerical values of all calculated parameters are given in *Table 1*. The necessary triplet levelshift

$$\Delta\varepsilon(\text{H}) = |\varepsilon(\text{H}) - \varepsilon(0)|, \quad (16)$$

would be of the order of  $3 \times 10^6 \text{ s}^{-1}$  for H = 4 Gauss, such that  $\Delta k_s(\text{H})/k_s(0) = 29\%$ , where again,  $\Delta k_s(\text{H}) = k_s(\text{H}) - k_s(0)$ . Since the decay constant  $k$  of the beating component, under the above assumptions, is independent of H and the overall decay is a superposition of slow exponential and beating contributions, the apparent

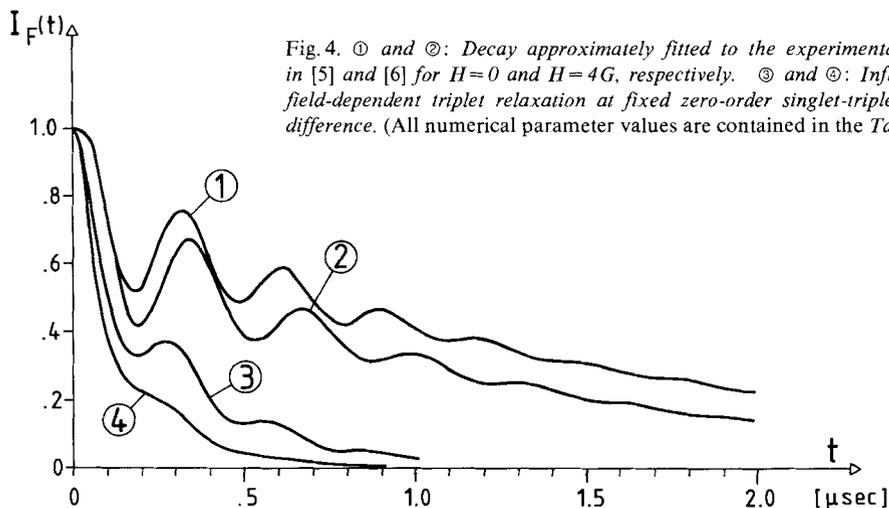


Fig. 4. ① and ②: Decay approximately fitted to the experimental results in [5] and [6] for  $H=0$  and  $H=4G$ , respectively. ③ and ④: Influence of field-dependent triplet relaxation at fixed zero-order singlet-triplet energy difference. (All numerical parameter values are contained in the Table).

net lifetime decreases roughly by about 30%, as is observed. *Henke et al.* have arrived at similar conclusions [6], however, using a triplet deactivation constant  $\beta \neq 0$  and getting a somewhat larger levelshift  $\Delta\epsilon(H) = 3.6 \times 10^6 \text{ s}^{-1}$  ( $\omega_{mn}$  in [6]). Now, the uncomfortable point in either case is that the resulting  $\Delta\epsilon$  is much too large for a triplet state of a molecule like biacetyl whose zero-field splitting parameters are reported to be  $D = -3.8574 \times 10^{10} \text{ s}^{-1}$ ,  $E = 0.3138 \times 10^{10} \text{ s}^{-1}$  [16], because the largest possible shift amounts to  $\Delta\epsilon = (E^2 + (\mu H)^2)^{1/2} - E = 7.89 \times 10^5 \text{ s}^{-1}$ , where  $\mu$  is twice the *Bohr* magneton [17]. The minimum shift is zero depending on which of the three triplet sublevels is coupled due to selection rules. This is true for a definite molecular orientation relative to the field. In general, all intermediate values are taken on since one would assume an isotropic distribution of molecular symmetry axis in the beam, all this being valid at least for high rotational quantum numbers. Thus, averaging the intensity  $I(\Delta\epsilon)$  over all possible orientations

Table. Numerical parameter values for the curves of Figure 4

Curve	1	2	3	4
Input parameters [ $10^6 \text{ s}^{-1}$ ]				
$\beta$	0	0	3	4
$\epsilon$	-16	-13	-16	-16
Calculated parameters				
$A_f$	0.0255	0.0398	0.0169	0.0157
$k_f$ [ $10^6 \text{ s}^{-1}$ ]	4.387	4.209	4.753	4.876
$A_s$	0.7640	0.7034	0.7673	0.7677
$k_s$ [ $10^6 \text{ s}^{-1}$ ]	0.613	0.791	3.247	4.124
$A_b$	0.2793	0.3225	0.2280	0.2197
$k$ [ $10^6 \text{ s}^{-1}$ ]	2.5	2.5	4.0	4.5
$\omega$ [ $10^6 \text{ s}^{-1}$ ]	21.197	19.018	21.250	21.258

For all cases:  $a = 5 \times 10^6 \text{ s}^{-1}$  and  $\lambda = 7 \times 10^6 \text{ s}^{-1}$ .

will yield a value  $\bar{I}$  corresponding to an average  $\bar{\Delta\varepsilon}$  lower than the above  $\Delta\varepsilon$  which is already too small. For low rotational quantum numbers, it does not make sense to speak about molecular orientation in general, but not even a careful consideration of details of rotational states as presented in [18] [19] for glyoxal will solve the problem since their main magnetic field dependence is related to the rotational magnetic moment which is generally smaller than  $D$  by more than three orders of magnitude [13].

This qualitative consideration is therefore sufficient for such low fields and again suggests that  $\beta$  should be field-dependent. However, a detailed interpretation of the mechanism responsible for the field dependence of the triplet deactivation constant  $\beta$  requires more experimental information. It would be interesting to check whether hot phosphorescence as already reported for biacetyl [14] could be associated with it and, if so, whether it also carries a beating component, as theoretically predicted [2].

In conclusion, low magnetic field experiments on molecules with strong zero-field splittings will always be difficult to interpret. One should try to go to high fields where the spin is decoupled from the molecular frame such that the dominant influence of the field is located in a linear levelshift. In general, one should not expect that the reported beat quenching with increasing field is a general phenomenon making any observation of beats at high fields impossible. This should also be clear from the level anticrossing experiments [20]. An other attractive possibility to avoid the problems of zero-field splitting and molecular orientation would be provided by experiments in electric fields where the associated linear and possibly quadratic *Stark* effects could yield more detailed information, particularly concerning the rotational states involved.

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