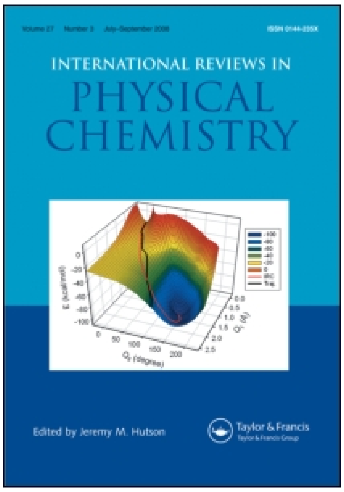

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Quantum beat spectroscopy of molecules

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Quantum beat spectroscopy of molecules

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This review deals with molecular high-resolution spectroscopy based on the quantum beat phenomenon. Applications of the essentially Doppler-free quantum beat technique are presented with special emphasis on the theoretical description. After an historical introduction and a general discussion of interference experiments, we discuss the expressions to describe the time-resolved fluorescence of a molecule following well defined laser excitation. Our general treatment for the characterization of the excited superposition state enables us to demonstrate the versatility of the method by identifying the excited molecular eigenstates with, for example, Zeeman levels or fine- and hyperfine-structure levels. In addition to the spectroscopic applications of quantum beat experiments in determining molecular structure parameters, we address the applications to molecular dynamics and statistical properties of molecular level structures.

1. Introduction

1.1. *Historical notes*

In 1923 fluorescence of mercury vapour was known to be polarized, but different workers had measured different polarization degrees. This discrepancy was experimentally resolved when Wood and Ellet (1923) showed that a weak magnetic field already strongly influences the polarization degree. Without a magnetic field, and the Earth's magnetic field carefully compensated, they observed an almost fully polarized resonance emission whilst the polarization was destroyed completely when a magnetic field of only two gauss, oriented perpendicular to the electric vector of the exciting light, was introduced. The authors argued that the Zeeman effect, known to resolve spectral lines into polarized components, would not manifest itself at such vanishingly small field strengths. Instead, they attributed their findings to a 'new magneto-optic effect, probably connected with the orientation of electron orbits in the magnetic field'.

In his work, Hanle (1923, 1924) explained Wood's observation by a precession of the radiating source atoms. Hanle (1925) recognized the relation to the Zeeman effect and interpreted the phenomenon, today known as the Hanle effect (Corney 1977), in terms of Bohr's quantum theory. Magnetic levels of a given electronic state, he argued, are well resolved by the Zeeman effect at high field but overlap at low field due to the life-time broadening. Under this condition neither a full energetic separation nor a complete directional quantization of the magnetic levels is possible. Hanle (1925) concluded that the transitions from different magnetic levels of the excited state 'can occur within a single atom and interfere with each other'. Consequently, the Hanle effect is due to a single particle interference.

Within the framework of Schrödinger's quantum theory the atom is said to be excited into a superposition of magnetic states which radiate coherently. The underlying theory of resonant light scattering was thoroughly developed by Breit (1933) in extending the work of Weisskopf and Wigner (1930). Figure 1 illustrates the

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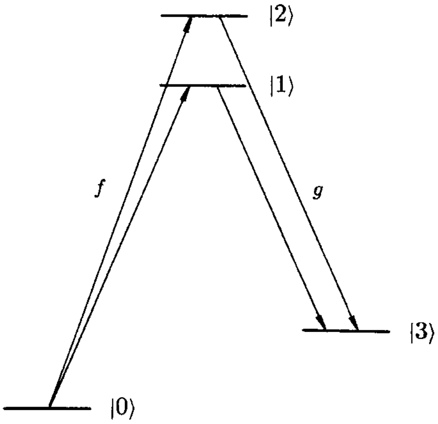


Figure 1. Diagram of a four level system. A photon with polarization $\boldsymbol{f}$ is absorbed by the ground state $|0\rangle$, excites a superposition of states $|1\rangle$ and $|2\rangle$, and is re-emitted with polarization $\boldsymbol{g}$, leaving the molecule in the final state $|3\rangle$.

situation where a photon of polarization $\boldsymbol{f}$ is absorbed by an atom in the ground state $|0\rangle$ and reemitted with polarization $\boldsymbol{g}$, leaving the atom in the final state $|3\rangle$. Breit (1933) derived expressions for the intensity and polarization of light in a resonance scattering process from well resolved or overlapping excited states ($|1\rangle$ and $|2\rangle$). His result was reformulated by Franken (1961) in his clear and concise explanation of level-crossing experiments (Colegrove *et al.* 1959). He assumed the first order time-dependent perturbation theory to be adequate and obtained for the state of the atom after pulse excitation the superposition

$$|\psi(t>0)\rangle = |0\rangle + \sum_{j=1}^{2} f_{j0} \exp(-\mathrm{i}(\omega_j - \mathrm{i}\Gamma/2)t)|j\rangle. \tag{1}$$

The states $|j\rangle$ of energy $\hbar\omega_j$ are excited with the probability amplitude f_{j0}, which is proportional to the transition dipole moment $\langle j|\boldsymbol{f\mu}|0\rangle$, and the states are exponentially damped by a common rate constant Γ (Franken 1961). The emission rate $R(\boldsymbol{f}, \boldsymbol{g}, t)$ for photons of polarization $\boldsymbol{g}$ is then

$$R(\boldsymbol{f}, \boldsymbol{g}, t) \sim |\langle 3|\boldsymbol{g\mu}|\psi(t)\rangle|^2$$

$$= \sum_{jj'} g_{3j} g^*_{3j'} f_{j0} f^*_{j'0} \exp(\mathrm{i}(\omega_{j'} - \omega_j)t - \Gamma t). \tag{2}$$

The interference effect is described by the terms with $j \neq j'$. It vanishes unless the two levels 'share' a photon in absorption and emission. The effect is termed quantum beat since the fluorescence intensity is modulated according to the frequency $\omega_{j'} - \omega_j$. This time dependence was not given explicitly by Breit (1933). Franken (1961) integrated the emission rate given by equation (2) with respect to time in order to obtain an expression adequate to the steady-state level-crossing experiment.

Before reviewing time-integrated and time-resolved (quantum beat) experiments in chapter 2 we discuss some general aspects of interference experiments in the next section.

1.2. *General aspects of interference experiments*

As depicted in figure 1 the excited atomic states act as radiation sources very much like the two slits in Young's interference experiment. After the detection of the photon, there is no way to decide from which source (slit) it has been emitted, since the final state of the atom is common to both emission channels. An interference effect is observed when a process occurs via two (or more) paths which are indistinguishable by the actual experimental arrangement, and which are associated with a well-defined relative phase. This phase relation is created by the excitation process and expressed by the superposition of the source states. Interference is always connected with the superposition principle which, in mathematical terms, is based on the linearity of the dynamical (Schrödinger-) equation governing the evolution of the system.

In describing an interference experiment the detection step must be taken into account since the experimental arrangement decides whether the interference effect is observed or not. For definiteness we treat the intensity measurement in a simple field-theoretic description (Walls 1977) where only two modes of the radiation field are considered. Denoting the state of the field by $|nm\rangle$ where n and m are the number of photons of the same polarization $\boldsymbol{g}$ in mode 1 and 2, respectively, the composed system can be described by a direct product of the atomic excited state and the vacuum state

$$\Psi(t=0)=[f_{10}|1\rangle+f_{20}|2\rangle]\otimes|00\rangle. \tag{3}$$

The atomic ground state, not being radiative, is not considered. In the course of time evolution the superposition of the atomic states is transferred to the field-states and the state of the composed system is

$$\begin{aligned}\Psi(t)&=|3\rangle\otimes[c_1(t)|10\rangle+c_2(t)|01\rangle]\\ c_j(t)&=g_{3j}f_{j0}\exp(-\mathrm{i}\omega_j t).\end{aligned} \tag{4}$$

As the measurement is performed on the field, the detection is expressed by Glauber's operator $\mathcal{E}^-\mathcal{E}^+$ (Glauber 1963), the relevant portion of which is given by

$$\mathcal{E}^-\mathcal{E}^+=(\kappa_1^*a_1^\dagger+\kappa_2^*a_2^\dagger)(\kappa_1a_1+\kappa_2a_2). \tag{5}$$

The $a_i[a_i^\dagger]$ are annihilation [creation] operators for photons in mode i and the κ_i denote time-independent proportionality constants. We do not specify them but interpret them as detector efficiency parameters for the corresponding modes. The intensity expected from the state in equation (4) is expressed as $I(t)=\langle\Phi(t)|\mathcal{E}^-\mathcal{E}^+|\Phi(t)\rangle$, reading

$$I(t)=|\kappa_1g_{31}f_{10}+\exp(-\mathrm{i}(\omega_2-\omega_1)t)\,\kappa_2g_{32}f_{20}|^2. \tag{6}$$

The detection operator $\mathcal{E}^-\mathcal{E}^+$ leads to the sum of two terms and is appropriate to describe an interference experiment. If we were to decide 'which path' the photon took, we would have to detect photons from one of the two modes, thus using $a_j^\dagger a_j$ instead of $\mathcal{E}^-\mathcal{E}^+$. No interference would show up since one path is blocked. In other words, the respective operators for measuring the interference pattern or the path do not commute and hence do not represent compatible measurements but complementary ones. This complementarity has been tested in 'which-way-experiments' using micromasers (Hellmuth *et al.* 1987, Scully and Walther 1989).

An equal probability for the two paths in equation (6) yields a complete modulation of the intensity while preference of one path over the other reduces the modulation depth. Thus, the relative probability for the processes $|0\rangle \rightarrow |1\rangle \rightarrow |3\rangle$ and $|0\rangle \rightarrow |2\rangle \rightarrow |3\rangle$ which depends on preparation (f_{j0}), emission (g_{3j}) and detection (κ_j) determines the modulation depth.

The restriction to one-photon states (Weisskopf and Wigner 1930) yields a one-to-one correspondence between the atomic and field states. Therefore, the intensity in equation (6) is given exclusively in atomic (and detector) variables like Franken's result in equation (2). This equation is put into the form

$$I(t) \sim |\langle 3|D|\psi(t)\rangle|^2, \tag{7}$$

where D is the detection operator. In some instances there exists a so-called 'doorway-state' (Rhodes 1983), i.e. a state $|s\rangle$ that is an eigenfunction of an operator which does not commute with the atomic Hamilton operator and that is the only state coupled to $|3\rangle$ by D. Then equation (7) simplifies to

$$I(t) \sim |\langle s|\psi(t)\rangle|^2. \tag{8}$$

This is the probability of finding the atom in the (nonstationary) state $|s\rangle$ at time t and the quantum beat is interpreted as a modulation of the $|s\rangle$ state population.

There have been attempts to interpret quantum beats as an interference effect from an ensemble of precessing dipoles radiating according to classical or neo-classical theories (Hanle 1924, Chow *et al.* 1975, Herman *et al.* 1975). The quantum mechanical single-particle interpretation is, however, conceptually much simpler and more versatile, being applicable to other than radiation effects (Hanle 1925, Podgoreckij and Chrustalev 1964, Dodd and Series 1978). There exist also quantum mechanical ensemble effects such as super-radiance or radiation trapping (Dicke 1954) but they will not be considered in this review. The single-particle nature of the superposition principle in quantum mechanics was observed in beam-experiments with low particle flows (Andra 1979) and is today tested directly with micromaser experiments (Walther 1988).

2. Quantum beat experiments

2.1. *Realization*

Using steady-state techniques to monitor the interference effect, the cross-terms in equation (2) are smoothed except those of degenerate states $|j\rangle$ and $|j'\rangle(\omega_j - \omega_{j'} = 0$: zero-frequency quantum beat). This fact is used in the level-crossing experiment (Colegrove *et al.* 1959, Franken 1961) where the signal as a function of the magnetic field strength shows resonances whenever the coherently excited Zeeman substates become degenerate. The special case of degeneracy at zero field gives rise to the Hanle effect (Corney 1977) mentioned above.

If the intensity of the exciting light is modulated a different resonance effect emerges whenever the modulation frequency matches the excited states energy separation $\omega_j - \omega_{j'}$ (Aleksandrov 1963, Corney and Series 1964b, Konstantinov and Perel 1964). For a discussion of this and other kinds of resonances the reader is referred to the review articles of Podgoreckij and Chrustalev (1964) and Zare (1971) on interference experiments, Happer and Gupta (1978) on level-crossing methods and Haroche (1976) and Aleksandrov (1978) on time-resolved (quantum beat) experiments.

A time-resolved experiment requires a preparation time of the superposition state which is well defined and short with respect to the quantum beat periods. Then, the excitation step can be separated from the subsequent free time evolution of the system.

These conditions are met by a short pulse excitation or by a sudden change in the environment such as the sudden application of an external field (Series 1964, Drake *et al.* 1975; see section 3.3).

Quantum beats in the fluorescence emission after light-pulse excitation had been predicted by Franken (1961) and Corney and Series (1964a) and were first observed by Aleksandrov (1964) and Dodd *et al.* (1964). Collisional excitation induced in crossed atom and electron beams has been used by Hadeishi and Nierenberg (1965) while Andrä (1970) introduced collisional excitation by passage of fast ion beams through thin carbon foils. The two techniques have been reviewed by Fowler (1979) and Andrä (1979), respectively.

The interest in molecular quantum beat spectroscopy arose with the advent of pulsed tunable dye lasers (Gornik *et al.* 1972, Schenck *et al.* 1973). In combination with high intensity and short pulse duration, dye laser systems provide the high selectivity required to prepare superposition states in a polyatomic molecule. Before addressing laser quantum beat spectroscopy in detail, some remarks on quantum beat detection are in order.

As expressed by equation (6), the interference effect is observed provided the detector efficiencies for both channels, κ_1 and κ_2, are not zero. Hence, every detection system that *assures the indistinguishability of the paths* can, in principle, be used as a measuring device for quantum beats. Recording the fluorescence from a superposition state (cf. section 1.2) is conceptually the simplest detection method. It can be performed by time-delayed photon detection, time-resolved emission measurement or by transforming the temporal modulation to a spatial one in a beam experiment. Beside these ‘passive’ methods based on spontaneous emission, ‘active’ detection techniques may be applied by which the superposition state is probed with an induced transition after a variable delay time. Along this line, modulations in *resonance absorption* from the excited superposition state were observed as a function of the delay of the probe laser pulse (Ducas *et al.* 1975) and *stimulated emission* techniques were used to probe quantum beats by Lange and Mlynek (1978) and Côte *et al.* (1989). Recently, Szatmari and Schäfer (1987) observed quantum beats in laser gain measurements which were shown to arise from coherences in the ground state of the laser medium (Walmsley *et al.* 1988).

Superpositions of highly excited, non-fluorescing Rydberg states are detected using bound-free transitions. These can be induced by sensitive photoionization (Zygan-Maus and Wolter 1978, Georges and Lambropoulos 1978) or field ionization techniques (Leuchs and Walther 1979). The quantum beats manifest themselves in the total number of electrons recorded as a function of the delay between excitation pulse and ionization pulse. Quantum beats are also predicted in molecular autoionization (Morgenstern 1987, Bordas *et al.* 1989) but have not yet been detected.

2.2. *Laser quantum beat spectroscopy*

For polyatomic molecules the laser quantum beat spectroscopy is the most powerful quantum beat technique and particularly convenient if the laser-excited superposition state can be monitored directly by fluorescence. Pulsed tuneable dye lasers in combination with cold molecular pulses from supersonic jets provide the favourable conditions for a selective, high-resolution molecular spectroscopy.

The laser pulse duration, usually in the ns to fs range, sets the time scale of the dynamical processes studied and it has to be shorter than the lifetime of the excited states, the quantum beat periods and the relaxation or dephasing times. On the other hand, the pulse length limits the spectral range in which molecular states are excited coherently. A Fourier-limited pulse of duration T_{pulse} has a coherent bandwidth of $\sim T_{\text{pulse}}^{-1}$ and coherent excitation of energy eigenstates is possible only if the pulse Fourier spectrum contains components at the appropriate frequencies (Franken 1961). Laser pulse coherence properties and their influence on the quantum beat signal have been discussed by several authors (Haroche 1976, Langhoff 1977, Silverman *et al.* 1978a, Sue and Mukamel 1984). These properties affect only the efficiency by which a superposition is created and not the beat frequency since the latter is given by the free molecular evolution. The information obtained from the beat frequencies is thus free from virtually all experimental parameters. Most important, there is essentially no Doppler effect owing to the fact that the quantum beat frequencies are very much smaller than the optical frequencies and saturation effects are negligible in broadband pulsed excitation (Silverman *et al.* 1978a).

Using a fast Fourier transform (FT) routine, the beat frequencies can readily be extracted from the signal. The real part of the FT reveals Lorentzian lines with a width of 2Γ given by the exponential decay constant at the frequencies 0, $\pm\nu_i$ (see figure 2). The resolution is thus lifetime-limited but can further be reduced by biasing the signal in favour of the long lived species of the ensemble (Krist *et al.* 1977, Dodd and Series 1978, Bitto and Huber 1990).

The expressions for the two-level superposition and the fluorescence intensity given in equations (1) and (2) are now extended to the more general form of multi-level excitation of a molecular ensemble

$$|\psi_g\rangle = |g\rangle + \sum_n \langle n|\mu\epsilon^L|g\rangle|n\rangle, \tag{9}$$

$$\begin{aligned} I(t) \sim \sum_g \rho_g \sum_f \kappa_f \sum_{nn'} &\langle f|\mu\epsilon^D|n\rangle\langle f|\mu\epsilon^D|n'\rangle^* \\ &\times \langle n|\mu\epsilon^L|g\rangle\langle n'|\mu\epsilon^L|g\rangle^* \exp\left(-\mathrm{i}(\omega_n-\omega_{n'})t-\tfrac{1}{2}(\gamma_n+\gamma_{n'})t\right). \end{aligned} \tag{10}$$

Similar formulae have been given by many authors (e.g. Franken 1961, Macek 1970, Haroche 1976, Luypaert and Van Craen 1977, Dodd and Series 1978, Hack *et al.* 1991). To also account for incoherent superposition of quantum beat signals from different ground states in the moleculer ensemble, we introduced the weighted summation (ρ_g) over g. Considering broad band excitation, the laser pulse Fourier components are not included explicitly. The first order transitions are determined by the dipole operator μ and the polarizations of the laser (ϵ^L) and the detector (ϵ^D). For different energy eigenstates different phenomenological damping rates γ_n are assumed.

The signal described by equation (10) corresponds to a sum of expectation values

$$I \sim \sum_g \rho_g\langle\psi_g|\Theta_{\text{det}}|\psi_g\rangle, \tag{11}$$

of the fluorescence monitoring operator

$$\Theta_{\text{det}} = \sum_f [\mu\epsilon^D]^\dagger|f\rangle\kappa_f\langle f|\mu\epsilon^D. \tag{12}$$

Expressed more generally, we write

$$I(t) \sim \mathrm{Tr}\,(\rho(t)\Theta_{\text{det}}) = \sum_{nn'} \langle n|\rho(t)|n'\rangle\langle n'|\Theta_{\text{det}}|n\rangle, \tag{13}$$

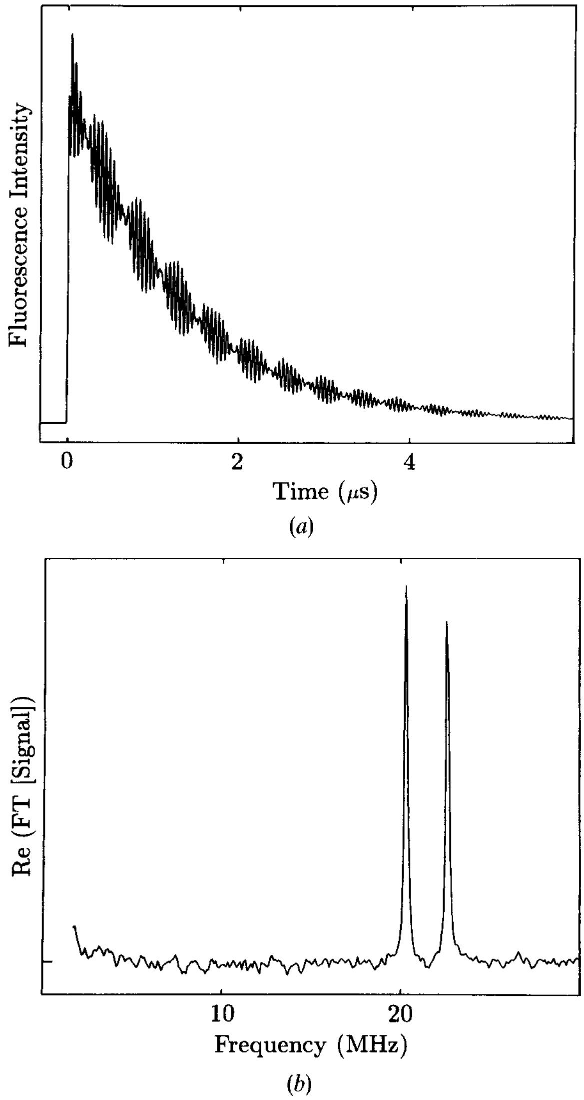


Figure 2. (*a*) Fluorescence decay with superimposed quantum beats. The experiment was performed on a rovibronic S_1 state of propynal. The real part of the Fourier transform (*b*) reveals two beat frequencies.

where the density matrix at time $t=0$ is given by

$$\rho(0)=\sum_{g} \mu\epsilon^{L}|g\rangle\rho_{g}\langle g|[\mu\epsilon^{L}]^{\dagger}. \tag{14}$$

The density matrix formulation (Barrat and Cohen-Tannoudji 1961) is used for general dynamical considerations and is indeed indispensable if relaxation mechanisms are rigorously treated (Lendi 1980, Kono *et al.* 1981, Schlag *et al.* 1982). The density matrix describing an open quantum system obeys the master equation

$$\dot{\rho}=-\mathrm{i}[H,\rho]-\tfrac{1}{2}\{\Lambda,\rho\}. \tag{15}$$

The first term corresponds to the free time evolution while the second accounts for damping, dissipation and dephasing phenomena which are observed in large molecules (cf. section 3.5). However, for spectroscopic evaluation of quantum beats equation (10) is sufficient and will be applied in the next chapter to various types of excited molecular states.

While equation (10) exhibits the interference character of the signal through the superposition state cross terms, it contains implicitly the spatial distribution of the resonance fluorescence through the polarization vectors. From the point of view of resonance scattering Mukamel and Jortner (1977) used the formalism of collision theory to describe the spatial redistribution of light after the scattering of a light wave packet. In spherical tensor notation, perturbation factors or perturbed angular correlations (Bosse and Gabriel 1974) are used and the isotropic and anisotropic radiation distribution after photon scattering is given by multipoles of rank smaller than two (cf. section 3.4). This technique is particularly powerful when molecular angular momentum states are considered (Fano and Macek 1973, Haroche 1976, Silverman *et al.* 1978b, Blum 1981).

3. Molecular quantum beat spectroscopy

3.1. *Preliminaries*

The laser quantum beat experiments reviewed in this chapter are discussed with regard to the nature of the closely spaced, coherently excited levels. Accordingly, sections 3.2 and 3.3 address quantum beats from Zeeman split levels which are induced by an external magnetic or electric field. The coherent excitation of fine or hyperfine levels without an external field is treated in section 3.4 and multilevel quantum beats in polyatomic molecules with emphasis on their dynamical and statistical features are discussed in section 3.5. For an account on experimental aspects of molecular quantum beat spectroscopy the reader is referred to a recent article by Bitto and Huber (1990).

3.2. *Pure Zeeman and Stark quantum beats*

Pure field-induced quantum beats arise from a superposition of magnetic sublevels of a single molecular state split by an external magnetic or electric field. The Hanle effect in mind, the first quantum beat experiments, were performed on Zeeman triplets of atoms (e.g. $^3P_1$-term of Cd: Aleksandrov 1964; $^3P_1$-term of Hg: Dodd *et al.* 1964; $^3P_1$-term of Yb: Gornik *et al.* 1972; $^1P_1$-level of Ba and Ca: Schenck *et al.* 1973) and the I_2 ($B^3\Pi_0$) molecule (Wallenstein *et al.* 1974). Figure 3 shows isolated states of angular momentum F which are split into $2F+1$ equally spaced sublevels due to the magnetic interaction

$$H_{\text{mag}} = -g_F\mu_B \boldsymbol{F}\cdot\boldsymbol{B}. \tag{16}$$

Taking the direction of $\boldsymbol{B}$ as the quantization axis, a laser pulse of σ-polarization ($\epsilon^L \perp \boldsymbol{B}$) will excite a superposition of levels $|FM_0 \pm 1\rangle$ from each of the ground state levels $|F_0M_0\rangle$. According to these $\Delta M = 2$ coherences and the linear Zeeman effect, the fluorescence will be modulated at the single frequency

$$\Delta\omega = 2g_F\mu_B B/\hbar, \tag{17}$$

that is twice the Larmor frequency. From pure Zeeman quantum beats the Landé g-factors of the excited angular momentum state can be extracted as demonstrated for atoms, diatomic molecules (I_2: Wallenstein *et al.* 1974; OH: Lebow *et al.* 1979) and for

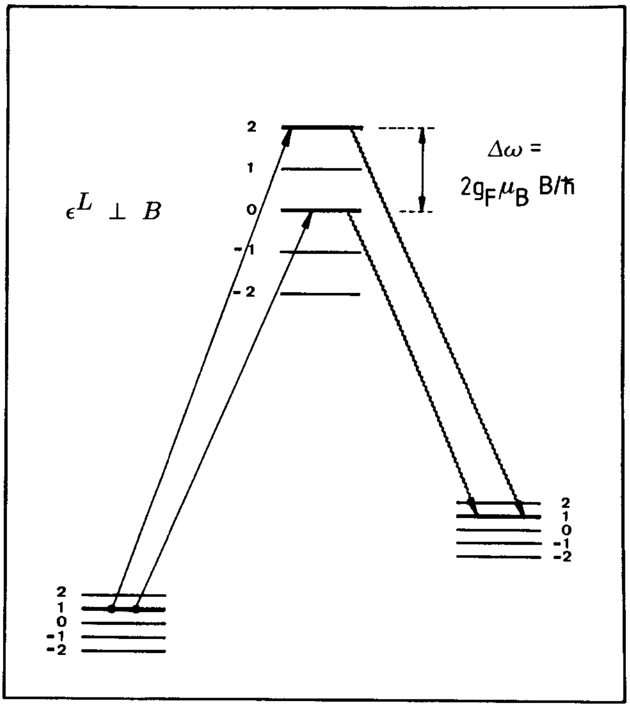


Figure 3. Zeeman quantum beats after σ-polarized excitation. The $\Delta M = 2$ quantum beats are illustrated by the coherent excitation of the states $|F=2, M=2\rangle$ and $|F=2, M=0\rangle$ from a ground state $|F=2, M_0=1\rangle$.

polyatomic molecules such as NO_2 (Brucat and Zare 1983), SO_2 (Watanabe *et al.* 1983a, b, 1985), CS_2 (Loge *et al.* 1986) and propynal HCCCHO (Dubs *et al.* 1986a).

At field strengths where the Zeeman splitting becomes comparable to the energy separation of molecular eigenstates (cf. figure 4) the off-diagonal elements induce appreciable mixing and, as a consequence, the linear tuning of magnetic levels is distorted. If spin-orbit coupling between Born–Oppenheimer singlet $|s_i\rangle$ and triplet $|t_l\rangle$ states is operative, the energy eigenvalues are obtained from the Hamilton matrix

$$H = \begin{pmatrix} E_i & v_{il} \\ v_{il}^* & E_l - g_l\mu_B MB/\hbar \end{pmatrix}. \tag{18}$$

In this case the Hamiltonian of equation (16) is not diagonal in the molecular eigenstate basis and Zeeman beat frequencies yield in addition to the Landé g-factors the coupling strength v_{il} as well as the zero-field separation of the molecular eigenstates (Dubs *et al.* 1986a). Moreover, from the time-resolved decay kinetics their lifetimes are obtained.

Quantum beats induced by an external *electric field* are in many respects closely related to Zeeman quantum beats. However, the Stark effect of an isolated angular momentum state is of second order and quadratic in the field strength $\mathscr{E}$ as opposed to the linear, first-order Zeeman effect. The energy shift E_{el} of a state $|JM\rangle$ due to the interaction

$$H_{el} = -\boldsymbol{\mu}\boldsymbol{\mathscr{E}}, \tag{19}$$

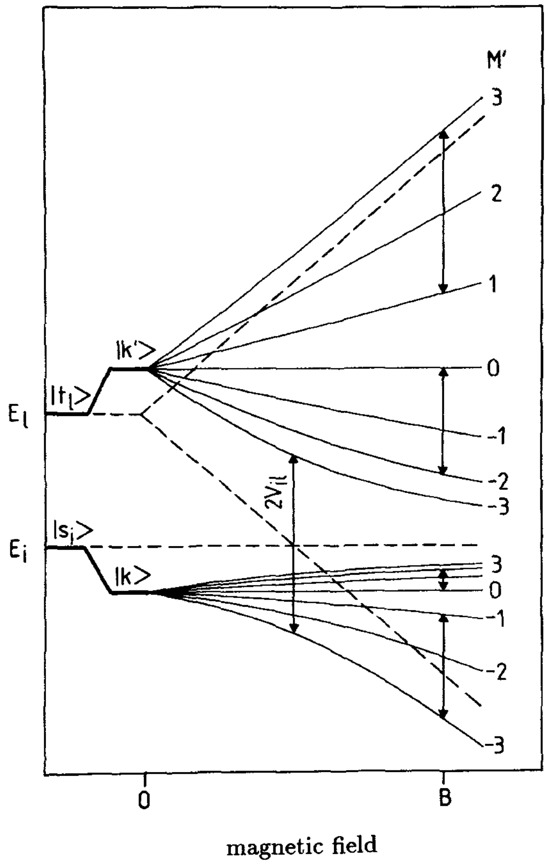


Figure 4. Zeeman effect on molecular eigenstates. Born–Oppenheimer singlet $|s_i\rangle$ and triplet $|t_l\rangle$ states show a linear Zeeman effect as indicated by the broken lines. The mixing of the two states by spin-orbit coupling results in the molecular eigenstates $|k\rangle$ and $|k'\rangle$ which tune (avoiding level crossings) as shown by the solid lines.

can generally be expressed by (Townes and Schawlow 1955)

$$E_{el}(J,M)=\sum_i (A_i(J)+B_i(J)M^2)\mu_i^2\mathscr{E}^2, \tag{20}$$

where μ_i is the projection of the dipole moment vector $\boldsymbol{\mu}$ on to the ith principal axis of the molecule. The factors A_i and B_i, expressed as perturbation series, contain the energetic separations to states coupled by μ_i and hence depend on the molecular structure parameters such as the rotational constants. Owing to the fact that states with equal $|M|$ remain degenerate and tune quadratically with the field strength $\mathscr{E}$, we observe $J-1$ different pure $\Delta M=2$ Stark quantum beat frequencies ($\epsilon^L \perp \mathscr{E}$) which are given by

$$\omega(M+2,M)=\sum_i B_i 4(M+1)\mu_i^2\mathscr{E}^2, \qquad 0\leqslant M\leqslant J-2. \tag{21}$$

Thus, given the experimental arrangement shown in figure 5, a regularly spaced multiplet of lines appears in the Fourier transform spectrum as displayed in figure 6.

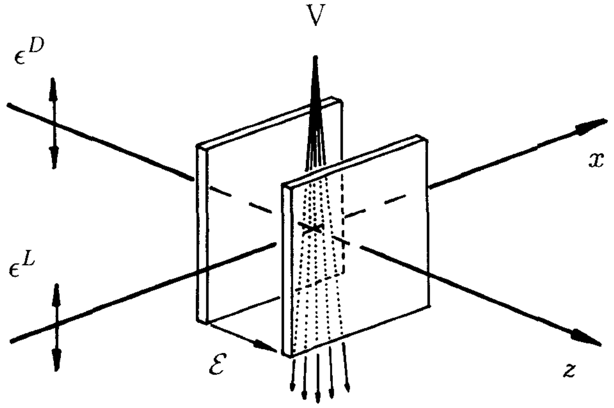


Figure 5. Experimental arrangement for measurements of Stark quantum beats. The laser beam, the detection axis and the molecular beam (expanding from valve V) are mutually orthogonal. The linear polarizations of the laser ϵ^L and the detector ϵ^D are chosen perpendicular to the field vector $\mathscr{E}$. The fluorescence is detected through a transparent electrode of the capacitor.

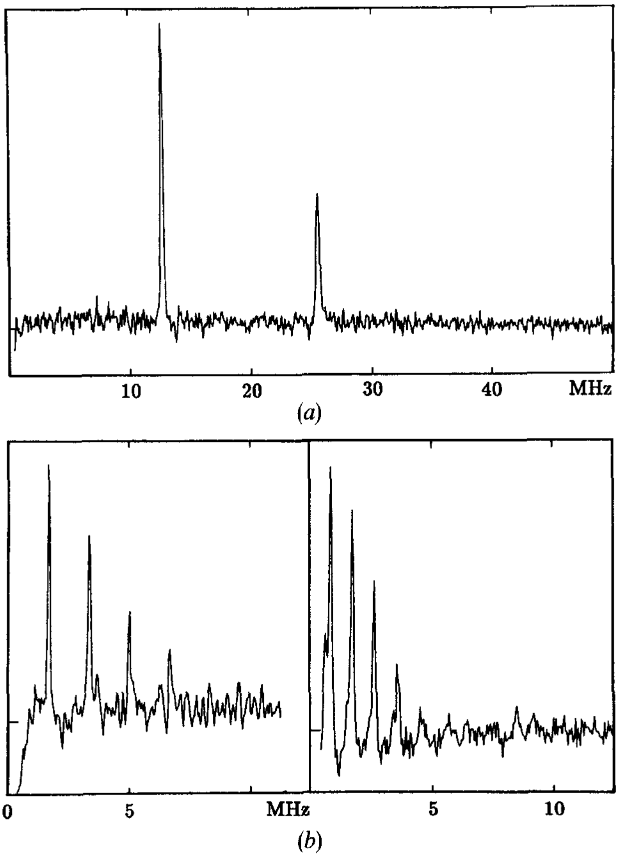


Figure 6. Spectra of pure $\Delta M = 2$ Stark quantum beats showing regularly spaced multiplets of lines. The measurements were performed on rotational states of deuterated propynal HCCCDO with (*a*) $J=3$, $\mathscr{E}=1{\cdot}5\,\mathrm{kV\,cm^{-1}}$, (*b*) $J=5$, $\mathscr{E}=2{\cdot}0\,\mathrm{kV\,cm^{-1}}$ and (*c*) $J=6$, $\mathscr{E}=2{\cdot}5\,\mathrm{kV\,cm^{-1}}$ (Hack *et al.* 1991).

Stark quantum beat spectroscopy, introduced to measure atomic polarizabilities (Hese *et al.* 1977), has been applied to determine the permanent electric dipole moment of molecules in different vibrational states. Diatomic molecules, having only one dipole component μ (along the internuclear axis) and a symmetric top rotational structure in $^1\Sigma$-states lend themselves for a direct analytic evaluation (Brieger *et al.* 1980 and 1983 on LiH and LiD; Brieger *et al.* 1981 on NaH; Schweda *et al.* 1985 on BaO; Büsener *et al.* 1987 on MgO). The Stark shifts are

$$\begin{aligned} E_{el}(J,M) &= (A(J)+B(J)M^2)\mu^2\mathscr{E}^2, \\ B(J) &= \frac{1}{B_v}\frac{3}{2J(J+1)(2J-1)(2J+3)}, \end{aligned} \tag{22}$$

where B_v is the rotational constant of the vibrational state $|v\rangle$. Obviously, the strongest tuning is observed with the lowest J-states.

Corresponding analytic expressions for the tuning coefficients of slightly asymmetric top molecules have been given by Hack *et al.* 1991, but, in general, the Stark tuning coefficients are calculated numerically. Dipole moments of electronically excited polyatomic molecules with C_{2v}-symmetry were measured by Vaccaro *et al.* (1989: H_2CO) and by Brucat and Zare (1985: NO_2) who used combined electric and magnetic fields. To determine a dipole moment vector that is not directed along one of the principal axes of the molecule, the fact is used that the Stark tuning of different rotational states depends to a different degree on the dipole vector components μ_i through the functions $B_i(J)$ in equation (20). Therefore, it is possible to determine magnitude *and* orientation of the dipole moment vector by analysing a set of selected rotational states. This approach was successfully used in the work on propynal in the S_1 electronic state (Schmidt *et al.* 1988).

Furthermore, the rotational constants of vibronically excited, short-lived species can be determined together with the dipole moment provided the theoretical expressions for the $B_i(J)$ are known. Such a selfconsistent determination of structure parameters has recently been performed on vibrationally excited S_1-propynal (Hack *et al.* 1991) and has demonstrated that quantum beat spectroscopy on a few selected rotational levels can provide molecular parameters with an accuracy that would require a long progression of rotational lines resolved beyond the Doppler width in frequency-domain spectroscopy.

3.3. *Quantum beats between states of opposite parity*

While for well-resolved dipole coupled levels a quadratic Stark effect is observed, almost degenerate levels with opposite parity show a linear Stark effect. This latter case is exemplified by the two fine structure levels $|s_{1/2}\rangle$ and $|p_{1/2}\rangle$ of hydrogen with energies $\hbar\omega_s$ and $\hbar\omega_p$, respectively. The presence of other fine structure levels and the hyperfine structure will not affect substantially the following arguments. Let Δ be the zero field separation of the two levels, i.e. the Lamb shift, and V the coupling matrix element

$$V=\langle s_{1/2}|\mu\mathscr{E}|p_{1/2}\rangle. \tag{23}$$

In the two-level approximation and after application of the field, the eigenstates may be written as

$$\begin{aligned} |\psi_1\rangle &= a(\mathscr{E})|s_{1/2}\rangle + b(\mathscr{E})|p_{1/2}\rangle, \\ |\psi_2\rangle &= -b(\mathscr{E})|s_{1/2}\rangle + a(\mathscr{E})|p_{1/2}\rangle, \end{aligned} \tag{24}$$

with the energy eigenvalues

$$E_{1,2}=\tfrac{1}{2}\hbar(\omega_s+\omega_p)\pm\tfrac{1}{2}(\Delta^2+4|V|^2)^{1/2}. \tag{25}$$

The field-induced parity mixing implies that transitions from the $|s\rangle$ ground state to both eigenstates $|\psi_{1,2}\rangle$ are allowed in the field and a linear Stark effect is predicted if $4|V|^2 \gg \Delta^2$. As a consequence, coherences can be created not only between m-levels of a single state $|\psi_i\rangle$ (pure Stark quantum beats) but also between the states $|\psi_1\rangle$ and $|\psi_2\rangle$. Thus, the beat frequencies provide the dipole component μ which connects the parity eigenstates and the separation Δ according to the Stark shifts given in equation (25). Hence, it is the symmetry-breaking effect of the electric field that makes zero-field parameters amenable to measurement.

The superposition of the eigenstates is prepared by laser excitation or alternatively by a sudden switching of the field by which the excited, metastable $|s_{1/2}\rangle$ state is quenched. In the latter case the superposition of excited states is described by the sudden transformation inverse to that of equation (24) rather than by the dynamical evolution during the excitation time. Interference experiments of this kind were suggested by Series (1964) in order to measure Lamb shifts and fine-structure separations and they have subsequently been performed in beam spectroscopy (Bashkin *et al.* 1965, van Wijngaarden *et al.* 1976).

A situation similar to that of hydrogen is met in diatomic molecules if they are excited into singlet states for which the coupling of molecular rotation $\boldsymbol{R}$ to the electronic angular momentum $\boldsymbol{L}(S=0)$ lifts the degeneracy in the internal projection quantum number $\pm\Lambda$ of the total angular momentum $\boldsymbol{J}=\boldsymbol{R}+\boldsymbol{L}$. The levels of such a Λ-doublet, denoted $|e\rangle$ and $|f\rangle$, have opposite parity and the Λ-splitting and dipole moment can be determined by Stark quantum beat experiments (Onishchuk and Podgoretskii 1968). For $^1\Pi$ states ($|\Lambda|=1$) the dipole matrix element V_M and the Λ-splitting Δ_{ef} to be inserted in equation (25) are given by (Derouard and Alexander 1986)

$$\begin{aligned} V_M&=\langle JMe|\boldsymbol{\mu}\boldsymbol{\mathscr{E}}|JMf\rangle=\frac{\mu\mathscr{E}M}{J(J+1)},\\ \Delta_{\mathrm{ef}}(J)&=qJ(J+1). \end{aligned} \tag{26}$$

Electric field mixing occurs for states with $|M|>0$ and, therefore, J different beat frequencies are expected after π-polarized coherent excitation of the Λ-doublet states (cf. figure 7(*a*)). According to equations (25) and (26) the beat frequencies are

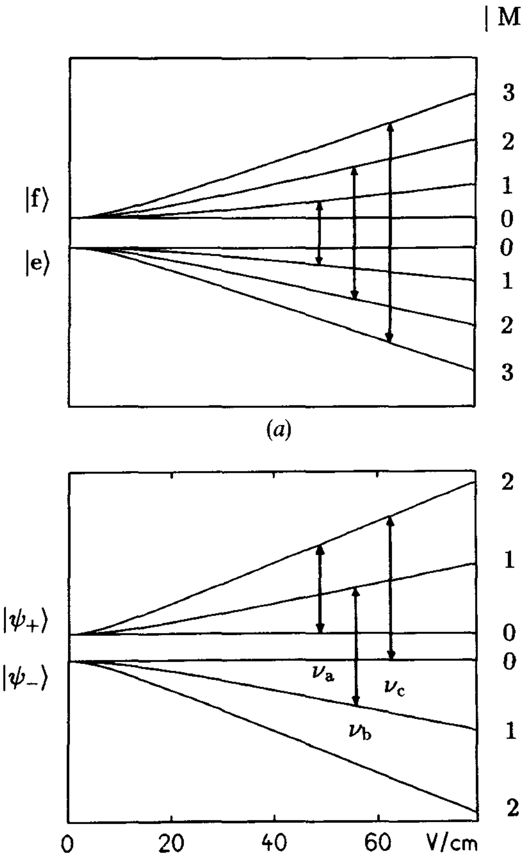
$$\nu_M=\frac{1}{h}(\Delta_{\mathrm{ef}}^2(J)+4|V_M|^2)^{1/2}, \tag{27}$$

and have been used by Derouard *et al.* (1989) to determine the vibrational dependence of μ and the Λ-doubling constant q of NaK ($\mathrm{B}^1\Pi$).

In asymmetric top molecules the states $|J\pm KM\rangle(K>0)$, degenerate in the symmetric top, are split by the 'asymmetry splitting' (Wang 1929, Herzberg 1966)

$$\Delta_K=(B-C)\left(\frac{B-C}{A-\frac{1}{2}(B+C)}\right)^{K-1}\frac{(J+K)!}{2^{4K-3}(J-K)!(K-1)!^2}, \tag{28}$$

to lowest order in $(B-C)/(A-\frac{1}{2}(B+C))$. The rotational constants $A\geqslant B\geqslant C$ are taken with respect to the principal axes of inertia a, b, c. The approximate eigenfunctions or



(*a*)

(*b*)

Figure 7. Stark quantum beats between states of opposite parity. (*a*) π-polarized excitation of Λ-doublet states with $J=3$ in an electric field gives rise to three $\Delta M=0$ beat frequencies as indicated by arrows. (*b*) σ-Polarized excitation of asymmetry doublet states with $J=2$ gives rise to the $\Delta M=2$ quantum beat frequencies denoted in accordance with equation (31). Only one of the two possible beats ν_a and ν_c are shown.

Wang functions of a near symmetric prolate top ($B\approx C$ in I^r-convention of King *et al.* 1943) are given by

$$|\psi_\pm\rangle=(\tfrac{1}{2})^{1/2}(|JKM\rangle\pm|J-KM\rangle). \tag{29}$$

These parity eigenstates are coupled by the electric interaction matrix element

$$V_M=\langle\psi_+|\mu\mathscr{E}|\psi_-\rangle=\mu_a\mathscr{E}\,\frac{MK}{J(J+1)}. \tag{30}$$

(Townes and Schawlow 1955). The two-level approach of equation (25) is valid for vibronic singlet states not being mixed to other rotational states. Schmidt *et al.* determined the asymmetry splitting (1987) and the dipole component μ_a (1988) of propynal HCCCHO and its deuterated isotopomer HCCCDO in different vibrational

S_1-states. The $\Delta M=2$ quantum beats of the asymmetry doublet states with $J=2=K$ have frequencies according to equation (25) and equations (28) to (30)

$$\begin{aligned} h\nu_a &= |E_\pm(M=2)-E_\pm(M=0)| = \tfrac{1}{2}(\Delta_2^2+4|V_2|^2)^{1/2}-\tfrac{1}{2}\Delta_2,\\ h\nu_b &= |E_\pm(M=1)-E_\mp(M=1)| = (\Delta_2^2+4|V_1|^2)^{1/2}, \qquad (31)\\ h\nu_c &= |E_\pm(M=2)-E_\mp(M=0)| = \tfrac{1}{2}(\Delta_2^2+4|V_2|^2)^{1/2}+\tfrac{1}{2}\Delta_2. \end{aligned}$$

The frequency ν_a corresponds to the pure $\Delta M=2$ quantum beat and is equal for both states $|\psi_{1,2}\rangle$ while ν_b and ν_c are due to coherences between these states. Figure 7 (*b*) shows the relevant level scheme, while the corresponding spectrum measured at two field strengths is displayed in figure 8. The asymmetry splitting is given by the frequency difference (Schmidt *et al.* 1987)

$$\Delta_2 = h(\nu_c-\nu_a), \qquad (32)$$

while the dipole component μ_a can be extracted from the relation (Hack *et al.* 1991)

$$|\mu_a\mathscr{E}| = \tfrac{3}{2}|V_2| = \tfrac{3}{2}h(\nu_a\nu_c)^{1/2}. \qquad (33)$$

It should be emphasized that no molecular parameters enter this direct measurement of $|\mu_a|$.

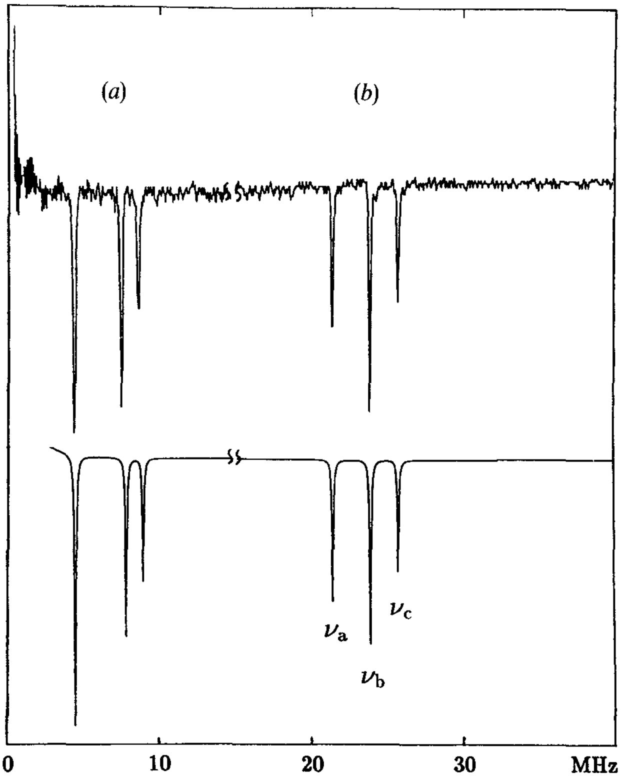


Figure 8. Measured (top) and calculated (bottom) Stark quantum beat spectra of an asymmetry doublet state $J=2$, $K=2$. The beats correspond to the level scheme depicted in figure 7 (*b*) and were measured on deuterated propynal HCCCDO at field strengths (*a*) $\mathscr{E}=20\ \mathrm{V\,cm^{-1}}$ and (*b*) $\mathscr{E}=80\ \mathrm{V\,cm^{-1}}$ (Huber 1990).

In concluding this section we would like to re-emphasize the high sensitivity of the quantum beat frequencies to the electric field strength as demonstrated in figure 8. It is, therefore, conceivable that quantum beats of selected states in molecules could be utilized as molecular 'optical voltmeters' for accurate *in situ* measurements of field strengths in plasma physics similar to the method reported by Moore *et al.* (1984).

3.4. *Fine-structure, hyperfine-structure and rotational quantum beats*

As opposed to the Stark and Zeeman quantum beats discussed above, fine- and hyperfine-structure quantum beats are observed without an external field (Macek 1969). These *zero-field quantum beats* reflect the 'natural splittings' due to intramolecular couplings of degenerate zero-order states. Hyperfine structure is caused by the coupling of nuclear spin $\boldsymbol{I}$ with electronic spin $\boldsymbol{S}$ through the classical dipole–dipole interaction of the associated magnetic moments and the quantum mechanical Fermi contact term. The latter is proportional to the electronic spin density at the nucleus and is expected to dominate whenever there is an appreciable contribution of σ-character to the electronic wave function.

Fine structure in atoms arises from electronic spin-orbit coupling. In poly-atomic molecules this interaction will affect triplet states ($S=1$) and it will couple singlet to triplet states since S is no longer conserved. Before we review quantum beat experiments guided by the underlying molecular level structure, we address the polarization and angular properties of the emitted fluorescence. Dealing with angular momentum superposition states, we adopt the spherical tensor notation which is particularly useful in the field-free case. To this end, we separate the angular momentum part $|jm\rangle$ from the molecular eigenfunctions $|n\rangle$, viz. $|n\rangle=|v\rangle|jm\rangle$, so that the fluorescence intensity described by equation (13) takes the form

$$I(t)\sim\sum_{vjm}\sum_{v'j'm'}\langle v;jm|\rho(t)|v';j'm'\rangle\langle v';j'm'|\Theta_{\mathrm{det}}|v;jm\rangle. \tag{34}$$

The dipole interaction $\boldsymbol{\mu\epsilon}$ appearing in the operators ρ of equation (14) and Θ_{det} of equation (12) is expressed in spherical tensor components as

$$\boldsymbol{\mu\epsilon}=\sum_{s}(-1)^{s}\mu_{-s}\epsilon_{s}. \tag{35}$$

For molecular problems the components of $\boldsymbol{\mu}$ are taken relative to a molecule fixed coordinate system rather than to the laboratory frame. If the rotation of the laboratory to the molecule fixed axes is described by the Eulerian angles $(\alpha\beta\gamma)$, which are taken as the dynamical variables of molecular rotation, the components μ_s are expressed as

$$\mu_s^{(\mathrm{lab})}=\sum_{r}\mu_r^{(\mathrm{mol})}\mathscr{D}^{1}_{sr}(\alpha\beta\gamma). \tag{36}$$

The component μ_r acts only on the vibronic part $|v\rangle$ of the molecular wavefunction while $\mathscr{D}^{1}_{sr}$ acts on $|jm\rangle$ which includes the rotational degrees of freedom. Applying the Wigner–Eckart theorem, the matrix elements of $\boldsymbol{\mu\epsilon}$ are factorized into a geometric part which contains the orientation quantum numbers and a reduced matrix element

$$\langle v;jm|\boldsymbol{\mu\epsilon}|v';j'm'\rangle=\sum_{s}(-1)^{s}\epsilon_{s}(-1)^{j-m}\begin{pmatrix} j & 1 & j'\\ -m & -s & m'\end{pmatrix}\langle v;j\,\|\mu\|\,v';j'\rangle, \tag{37}$$

with the phase convention adopted from Lindner (1984). In view of equation (36) the reduced matrix element for molecules can further be decomposed into a vibronic and an angular momentum part

$$\langle v; j \| \mu \| v'; j' \rangle = \sum_r \langle v|\mu_r|v'\rangle \langle j \| \mathscr{D}^1_r \| j' \rangle, \tag{38}$$

where the subscript r on $\mathscr{D}^1$ indicates that the matrix element is not yet reduced with respect to the internal orientation.

The matrix elements of the detection operator Θ_{det} of equation (12) will be separated similar to the ones given in equation (37). Assuming that the detection efficiency κ_f does not depend on m_f, the sum

$$\sum_{v_f j_f} \sum_{m_f} |j_f m_f\rangle \kappa_{v_f j_f} \langle j_f m_f|, \tag{39}$$

constitutes a scalar operator (Fano and Macek 1973) and the polarization and dipole operators in Θ_{det} can be recoupled to give

$$\Theta_{\text{det}} = \sum_{Qq} P^{Q*}_q(\epsilon^D) M^Q_q(f). \tag{40}$$

Casting its matrix elements into the form

$$\langle v'; j'm' | \Theta_{\text{det}} | v; jm \rangle = \sum_{Qq} P^{Q*}_q(\epsilon^D) \times (-1)^{j'-m'} \begin{pmatrix} j' & Q & j \\ -m' & q & m \end{pmatrix} \langle v'; j' \| M^Q(f) \| v; j \rangle. \tag{41}$$

the polarization tensor (cf. table 1) is given by (Lindner 1984)

$$P^Q_q(\epsilon) = 3^{1/2} \hat{Q} \sum_{ss'} (-1)^{1+s} \epsilon_s \epsilon^*_{s'} \begin{pmatrix} 1 & 1 & Q \\ -s & s & q \end{pmatrix}, \tag{42}$$

Table 1. Explicit expressions for the polarization tensors, defined in equation (42).

P^0_0	1
P^1_0	$(\frac{3}{2})^{1/2} \cos \Theta P_3$
P^1_1	$-(\frac{3}{4})^{1/2} (\sin \Theta \exp(\mathrm{i}\Phi)) P_3$
P^2_0	$(\frac{1}{4})^{1/2} (1 - \frac{3}{2} \sin^2 \Theta (1 + P_1))$
P^2_1	$-(\frac{3}{4})^{1/2} \sin \Theta \exp(\mathrm{i}\Phi)(\cos \Theta (1 + P_1) + \mathrm{i} P_2)$
P^2_2	$(\frac{3}{16})^{1/2} \exp(2\mathrm{i}\Phi)(\sin^2 \Theta - (1 + \cos^2 \Theta) P_1 - 2\mathrm{i} \cos \Theta P_2)$
$P^Q_{-q} = (-1)^q P^{Q*}_q$	

The angles (Θ, Φ) fix the direction of the photon propagation. The transverse polarization is expressed through the Stokes parameters P_1, P_2 and P_3 with which the polarization density matrix reads

$$\frac{1}{2} \begin{pmatrix} 1 + P_3 & -P_1 + \mathrm{i} P_2 \\ -P_1 - \mathrm{i} P_2 & 1 - P_3 \end{pmatrix}.$$

The special case of linear polarization ($P_3 = 0$) or left and right circular polarization ($P_3 = \pm 1$, $P_1 = 0 = P_2$) are readily obtained.

and the reduced matrix element is obtained as

$$\langle v';j'\|M^Q(f)\|v;j\rangle=\frac{(-1)^{j+j'+1}}{3^{1/2}}\,\hat{Q}$$

$$\times\langle v';j'\|\mu\|v_f;j_f\rangle\kappa_{v_fj_f}\langle v_f;j_f\|\mu\|v;j\rangle\begin{Bmatrix} j' & j & Q \\ 1 & 1 & j_f\end{Bmatrix}. \tag{43}$$

In molecular applications this expression can further be rearranged by applying equation (38).

A decomposition completely analogous to equation (41) can be given for the matrix elements of $\rho(t)$ in equation (34) after laser excitation, provided the ground state population is isotropic

$$\langle v;jm|\rho(0)|v';j'm'\rangle=\sum_{Q'q'}P^{Q'*}_{q'}(\epsilon^L)$$

$$\times(-1)^{j-m}\begin{pmatrix} j & Q' & j' \\ -m & q' & m'\end{pmatrix}\langle v;j\|M^{Q'}(g)\|v';j'\rangle. \tag{44}$$

For the corresponding tensorial decomposition of $\rho(0)$ following impact excitation of atomic fine- and hyperfine-structure beats the reader is referred to Ellis (1973) and Fano and Macek (1973).

Without an external field the energy eigenvalues are degenerate with respect to the m-quantum numbers and the explicit dependence on m and m' in equation (34) can be eliminated using the orthogonality relation for the $3j$-symbols appearing in equations (41) and (44). The expression for the fluorescence equation (34), then, takes the form

$$I(t)=\sum_{Qq}(-1)^q P^Q_{-q}(\epsilon^D)P^Q_q(\epsilon^L)\sum_{vj}\sum_{v'j'}\delta(jj'Q)$$

$$\times\langle v;j\|M^Q(g)\|v';j'\rangle\langle v';j'\|M^Q(f)\|v;j\rangle$$

$$\times\exp(-\mathrm{i}(\omega_{vj}-\omega_{v'j'})t-\tfrac{1}{2}(\gamma_{vj}+\gamma_{v'j'})t). \tag{45}$$

The polarization and the spatial distribution of the emitted fluorescence are expressed by the scalar product

$$\Pi^0_0(Q;\epsilon^D,\epsilon^L):=\sum_q(-1)^q P^Q_{-q}(\epsilon^D)P^Q_q(\epsilon^L),\qquad Q=0,1,2. \tag{46}$$

which is independent of molecular variables. This expression has been derived and discussed by Luypaert and van Craen (1977) and others. Its main features are as follows:

(1) Isotropic emission ($Q=0$) is due to states with equal angular momenta ($j=j'$) according to the triangular condition $\delta(jj'Q)$. It is unpolarized since $\Pi^0_0(0;\epsilon^D,\epsilon^L)=1$ and unmodulated for the diagonal terms ($v=v'$). However, states of different energy ($v\neq v'$) give rise to modulations which are called *molecular quantum beats* (see figure 9).

(2) Polarization tensors of rank $Q=1$ represent circularly polarized light (cf. table 1). Only the angle Θ enclosed by the directions of the laser beam and towards the detector is relevant for the angular distribution

$$\Pi^0_0(1;\epsilon^D,\epsilon^L)=\pm\tfrac{3}{2}\cos\Theta. \tag{47}$$

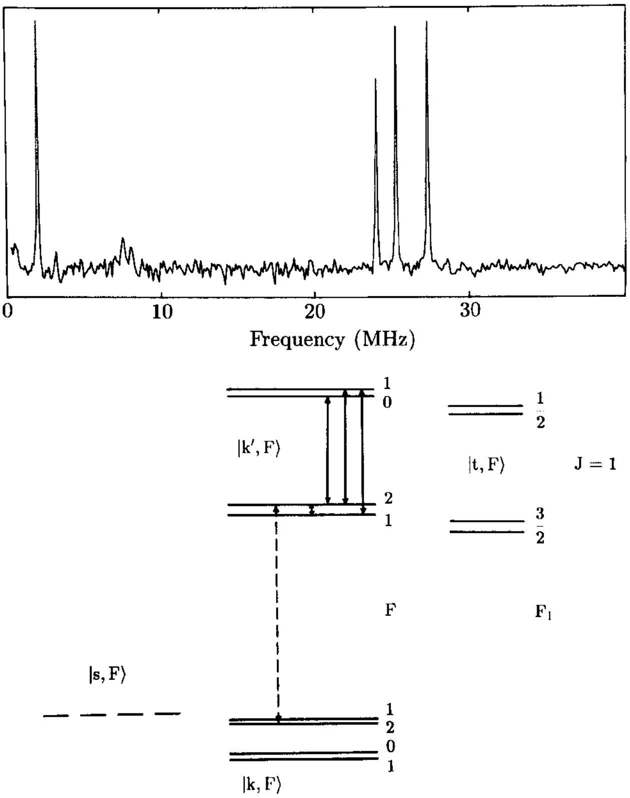


Figure 9. Hyperfine quantum beats. The level scheme illustrates the mixing of Born–Oppenheimer hyperfine levels of a singlet $|s,F\rangle$ and a triplet $|t,F\rangle$ state to molecular eigenstates $|k,F\rangle$ and $|k',F\rangle$ by spin-orbit interaction. The hyperfine-coupling follows Hund's case $b_{\beta J}$ in which two inequivalent nuclear spins are coupled in sequence to $J=1$ to give $F_1=J\pm 1/2$ and $F=F_1\pm 1/2$. Isotropic *molecular quantum beats* between states $|k,F\rangle$ and $|k',F\rangle$ with equal F quantum numbers are exemplified by the dashed arrow. The full arrows represent polarized hyperfine quantum beats illustrated by the spectrum on the top which was obtained from the predominantly triplet eigenstate $|k',F\rangle$ (Bitto *et al.* 1990). The four lines correspond to coherencies obeying the triangular condition $|F-F'|\leqslant Q=2\leqslant F+F'$ imposed by the linear polarizations.

The sign reflects the relative circular polarization. Thus, right and left circular polarized emissions are opposite in phase and no beats are observed in unpolarized detection. Owing to the Θ dependence of the radiation pattern, the total polarized emission is also unmodulated.

(3) The aligned contribution ($Q=2$) can be expressed as

$$\Pi_0^0(2;\epsilon^D,\epsilon^L)=A(1-\tfrac{3}{2}\sin^2\Theta^D(1+\cos 2\phi^D)). \tag{48}$$

If the laser is circularly polarized, then $A=1/2$ and Θ^D refers to the laser beam direction; if the laser is linearly polarized, then $A=-1$ and Θ^D refers to the polarization direction. In this case the result is commonly expressed by the Legendre polynomial

$$\Pi_0^0(2;\epsilon^D,\epsilon^L)=2P_2(\cos\Theta^{DL}), \tag{49}$$

where Θ^{DL} refers to the relative orientation of the linear polarizations. Modulations can be observed with an unpolarized or circularly polarized detector (when $\cos 2\phi^D = 0$) except for the magic angle $\Theta^D = 54{\cdot}7^\circ$. With a linear detector polarization the modulation is suppressed for the magic angle between ϵ^D and the reference axis defined as above. The total aligned emission is unmodulated.

(4) Expression (46) transforms like a scalar since we started from an isotropic molecular sample prior to excitation. If the molecules were aligned, however, tensors Π_k^K of rank $0 \leqslant K \leqslant 4$ would appear. This situation, commonly met in LIF experiments, is discussed by Greene and Zare (1983).

(5) The presence of a homogeneous external field destroys the isotropy but preserves axial symmetry. Therefore, tensors Π_0^K will appear in the corresponding expression as discussed by Hese *et al.* (1977) and Hack *et al.* (1991).

The modulation of the vector and tensor parts ($Q = 1, 2$) of the emission mirrors the modulation of the matrix elements of the tensor $M^Q(f)$. Relating these matrix elements to orientation and alignment, Fano and Macek (1973) interpreted them as expectation values of angular momentum operators, thereby tracing the modulation to a reversible exchange of angular momentum between internal degrees of freedom. Recalling, for example, that $\boldsymbol{F} = \boldsymbol{J} + \boldsymbol{I}$ is a constant of the motion, the measured periodic loss of the electronic orientation $\langle \boldsymbol{J} \rangle$ must be compensated by a periodic gain in the unobserved nuclear spin orientation $\langle \boldsymbol{I} \rangle$ which oscillates 180° out of phase.

We now turn to specific fine- and hyperfine-structure quantum beats. For problems involving fine-structure, the atomic states $|jm\rangle$ introduced in equation (34) are identified with $|(LS)JM_J\rangle$. An extensively studied example of these fine-structure zero-field quantum beats (Haroche 1976) are Rydberg D states of sodium ($L = 2$; $J = \frac{3}{2}, \frac{5}{2}$) which are coherently prepared by two-step laser excitation (Haroche *et al.* 1974). The measurements yielded fine-structure intervals and, in conjunction with an electric field, the ordering of the fine-structure levels (Fabre *et al.* 1975) and their strong polarizability (Fabre and Haroche 1975). These experiments have been analysed in a more general context by Silverman *et al.* (1978b).

Atomic hyperfine-structure quantum beats have been used by Haroche *et al.* (1973) to demonstrate the power of the method in determining hyperfine-structure splittings. The relevant formula for the signal has been derived by Luypaert and van Craen (1977) and it parallels equation (45) for the substitution $|jm\rangle \rightarrow |(JI)FM_F\rangle$. For fixed J and I values the beats are modulated with frequencies $\omega_F - \omega_{F'}$. Theoretical expressions for these energy differences allowed Krist *et al.* (1977) to determine the magnetic interaction constant and the nuclear quadrupole moment responsible for the hyperfine-structure in sodium.

For molecules the representation of hyperfine states does not often follow a simple algebraic coupling scheme. Should spin-orbit and hyperfine interactions be comparable in strength, J is no longer a good quantum number and an explicit diagonalization of the Hamilton matrix is mandatory. If, however, one of Hund's coupling cases is adequate, the evaluation of the reduced matrix elements in equation (45) is possible by means of Wigner transformations. This has been illustrated for Hund's case $b_{\beta J}$ where two inequivalent nuclear spins are coupled in sequence to give the total angular momentum and where the states $|jm\rangle$ are represented by (Dubs *et al.* 1985)

$$|(((NS)JI_1)F_1I_2)FM_F\rangle. \tag{50}$$

Equation (45) was used in an experiment by Dubs *et al.* (1986b) on the excited levels $|(((10)1\frac{1}{2})F_1\frac{1}{2})FM_F\rangle$ of propynal and was found to describe the polarization behaviour very well.

The coupling scheme of equation (50) fails if spin-orbit interaction mixes hyperfine levels of singlet (S_1) and triplet (T_1) states to molecular eigenstates. Under these circumstances, illustrated in figure 9, an analytic description of the beat frequencies requires the knowledge of all zero order states involved in order to determine the eigenvalues of the Hamilton matrix. This was performed successfully by Bitto *et al.* (1990) for the determination of pure triplet dipole–dipole and Fermi contact coupling constants in propynal. The hyperfine quantum beats measured in the predominantly triplet eigenstate by these authors are reproduced in figure 9.

In dense molecular spectra hyperfine levels of different molecular eigenstates $|k\rangle$ and $|k'\rangle$ are easily excited coherently and, as discussed above, molecular quantum beats between states of equal F-values can be observed. These beats were used by Dubs *et al.* (1985) to measure singlet–triplet coupling matrix elements between zero-order states $|s; FM_F\rangle$ and $|t; FM_F\rangle$. In addition, the introduction of a magnetic field allowed them to determine g-values in much the same way as discussed in section 3.2 in connection with pure Zeeman quantum beats (Mühlbach *et al.* 1984, Dubs *et al.* 1985). Assuming a linear Zeeman effect the quantum beat frequencies tune in accordance to

$$\hbar\omega_F(B, M_F) = \hbar\omega_F(0) + \mu_B|g_k - g_{k'}|M_F B. \tag{51}$$

Figure 10 illustrates the situation for two states with $F=2$ coupled to molecular eigenstates which are split in the magnetic field $\boldsymbol{B}$.

Finally, we highlight the application of equation (45) in connection with pure rotational quantum beats where the states $|jm\rangle$ are symmetric top $|JKM\rangle$ or

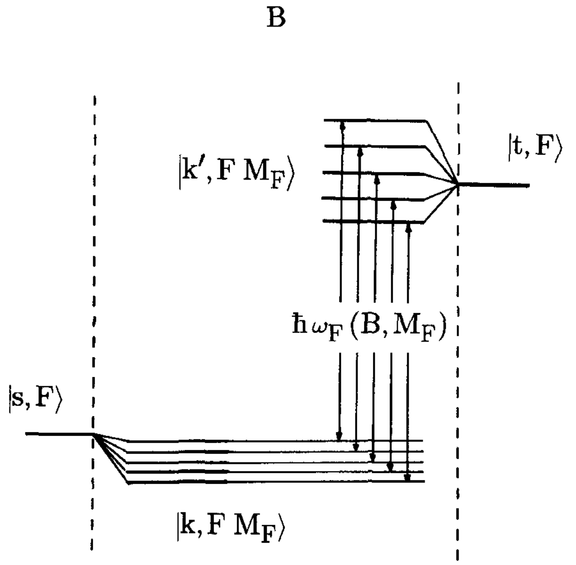


Figure 10. Zeeman effect on molecular quantum beats. The example shown corresponds to the *molecular quantum beat* between states of $F=2$ indicated by the dashed arrow in figure 9. The magnetic field B splits the Zeeman sublevels $|k, F\,M_F\rangle$ of the eigenstates according to their g-values giving rise to $(2F+1)$ different beat frequencies ω_F.

asymmetric top $|J\tau M\rangle$ functions (Felker and Zewail 1987). Starting from a ground state $|J_0K_0M_0\rangle$, a superposition of states $|JKM\rangle$ can be excited where $J=J_0, J_0\pm 1$ and, in the case of a parallel type transition, $K=K_0$. The three expected beat frequencies are $\nu_1=2(J_0+1)B$, $\nu_2=2J_0B$ and $\nu_3=\nu_1+\nu_2$ when expressed by the rotational constant B. Since in large molecules the rotational structure is very dense, many ground state levels J_0 will be populated even for molecules cooled by free jet expansion. Thus, the observed signal is an incoherent superposition of many beat patterns from different ground states. Although the beat frequencies are different, they are integer multiples of the fundamental $\nu^{(0)}=2B$. This fact gives rise to constructive interferences (recurrences) at times $t_n=n/2B$ or $t_n=n/(B+C)$ for slightly prolate top molecules as was demonstrated in the fluorescence decay of *t*-stilbene (Felker *et al.* 1986, Baskin *et al.* 1986, Baskin *et al.* 1987). It should be noted that the recurrences here are due to the ensemble average and not due to single molecule interference.

3.5. *Multilevel quantum beats*

The applications of molecular quantum beats discussed so far were of a spectroscopic nature. The determination of molecular structure parameters and intramolecular coupling constants extracted from quantum beat frequencies required a theoretical description of the excited level structure in terms of these parameters. Zero-field quantum beats of polyatomic molecules, however, are often difficult to interpret since the assignment of the levels involved and even the nature of the coupling between these levels is uncertain. To each Born–Oppenheimer singlet excited state $|s\rangle$ there corresponds a set of molecular eigenstates $\{|n\rangle\}$ as a result of the intramolecular coupling to a set of quasi isoenergetic Born–Oppenheimer 'dark' background states $\{|l\rangle\}$. Expanding the molecular eigenstates as

$$|n\rangle = c_{sn}|s\rangle + \sum_{l=1}^{N} c_{ln}|l\rangle, \tag{52}$$

we may take the number N of interacting states to characterize the 'spectroscopic environment' of state $|s\rangle$. In the 'small molecule' limit (Robinson 1967), N is a small number and excitation of state $|s\rangle$ involves only one or a few molecular eigenstates. Hence, the exponential decay of the fluorescence will contain a few (if any) oscillations which appear as well-resolved lines in the quantum beat spectrum. In the 'large molecule' limit, N is large so as to correspond to a continuous set of background levels. The decay, showing no distinct oscillations, will be accelerated owing to the dissipative nature of the continuum. By means of time-resolved recording of the fluorescence, energy flow and internal vibrational energy redistribution (IVR) to non-radiative, dissipative degrees of freedom can be directly studied (Freed and Nitzan 1980, Felker and Zewail 1988).

In the following, the case between the 'small' and 'large' molecule limits, the so-called 'intermediate' case, is considered. In spite of the fact that polyatomic molecules in the excited S_1-state have a high density of background S_0- or T_1-states, they still can display 'small' or 'intermediate' molecule behaviour. This indicates that in addition to dissipative continua a finite number N of non-radiative, non-decaying background states strongly couple to the excited rovibronic singlet state (Nitzan and Jortner 1972, Jortner and Mukamel 1974, Tramer and Voltz 1979). Adapting equation (45) to molecular quantum beats (as mentioned in item (1)), we obtain

$$I(t)=\sum_{vj}\sum_{v'j'}\delta(jj'0)\langle vj\,\|M^0(g)\|v'j'\rangle\langle v'j'\|M^0(f)\|vj\rangle$$
$$\times\exp(-\mathrm{i}(\omega_{vj}-\omega_{v'j'})t-\tfrac{1}{2}(\gamma_{vj}+\gamma_{v'j'})t). \tag{53}$$

Since by assumption only the singlet part $|sj\rangle$ of the molecular eigenstate of equation (52) is coupled to the ground state, the reduced matrix element is given by

$$\langle v'j'\|M^0\|vj\rangle=c^*_{sj;\,v'j}c_{sj;\,vj}\langle sj\,\|M^0\|sj\rangle, \tag{54}$$

and is proportional to the 'singlet character' of the eigenstates involved. The remaining matrix element, being diagonal in s and j, is real. Hence, the fluorescence equation (53) is expressed as

$$I(t)=\sum_j\langle sj\,\|M^0(g)\|sj\rangle\langle sj\,\|M^0(f)\|sj\rangle$$
$$\times\sum_{vv'}|c_{sj;\,v'j}|^2|c_{sj;\,vj}|^2\cos(\omega_{vj}-\omega_{v'j})t\exp(-\tfrac{1}{2}(\gamma_{vj}+\gamma_{v'j})t). \tag{55}$$

The sum over j reminds us of the fact that the beat pattern is very often an incoherent superposition of decays from states with different j quantum numbers, e.g. from hyperfine structure. A sum over s is absent since we considered excitation of a single Born–Oppenheimer state. Moreover, the broad-band assumption implicit in the derivation of equation (53) is equivalent to the excitation of the 'doorway state' $|s\rangle$ (Rhodes 1983) since, for $t=0$, each of the sums over v and v' is unity. If, however, the 'spread of oscillator strength' is comparable to the coherence width of the laser, the pulse properties must properly be taken into account.

For the subsequent discussion we split the sum over v and v' in equation (55) into unmodulated and modulated parts and dismiss the sum over j

$$I(t)\sim\sum_n|c_{sn}|^4\exp(-\gamma_n t)$$
$$+\sum_{n\neq n'}|c_{sn'}|^2|c_{sn}|^2\cos(\omega_n-\omega_{n'})t\exp(-\tfrac{1}{2}(\gamma_n+\gamma_{n'})t). \tag{56}$$

The damping rates γ_n are, in general, given by complex expressions involving the matrix elements of H and Λ in the master equation (15) as shown for a simple model system by Lendi (1980).

In the weak coupling case, the singlet character is concentrated on one particular eigenstate, say $|n=0\rangle$, whence

$$|c_{s0}|^2\approx 1,\qquad |c_{sn}|^2\ll 1,\qquad n>0. \tag{57}$$

Then equation (56) reduces to

$$I(t)\sim|c_{sn}|^2\exp(-\gamma_0 t)+2\sum_{n>0}|c_{sn}|^2\cos(\omega_n-\omega_0)t\exp(-\tfrac{1}{2}\gamma_0 t). \tag{58}$$

Accordingly, the modulation depth is proportional to $|c_{sn}|^2$ and provides the coupling matrix elements in lowest order perturbation theory (Chaiken *et al.* 1981a, Stafast *et al.* 1983).

Depending on the nature of the background states, the intramolecular coupling is due to vibronic interaction or spin-orbit interaction. Beats induced by internal conversions (S_1-S_0 interaction), detectable only in small molecules where the state density is not too high, have been reported for SO_2 (Sharfin *et al.* 1982, Ivanco *et al.* 1983). More frequently, beats in polyatomic molecules are due to intersystem crossing (S_1-T_1 interaction). Assuming that an individual rovibronic singlet level couples to N triplet levels the fluorescence decay of equation (56) will exhibit $N(N+1)/2$ distinct beat frequencies corresponding to the energy differences between the $N+1$ eigenstates involved. The complexity of the beat spectrum is, therefore, a direct measure of the number N and *quantum beats can be used as a state counting method.* The three-level case ($N=2$), for example, will yield three frequencies, one of which is just the sum of the other two, a feature very similar to the one observed in hyperfine-structure beats (Haroche *et al.* 1973) (for an instructive example see, e.g., van der Meer *et al.* 1982). If combination frequencies can be identified in the quantum beat spectrum and their relative intensities match the conditions imposed by equation (56) the underlying level structure can eventually be recovered in a way similar to that used in high-resolution absorption spectroscopy (Kommandeur 1988). The limitation to this combinatory procedure is imposed by the unknown number of incoherently superposed quantum beat decays.

The appearance of more and more lines in the quantum beat spectrum with increasing N reflects the increasing number of cosine terms in the time evolution of equation (56). At $t=0$ all these terms add constructively, but shortly afterwards they interfere destructively due to the phase mismatch of the many different frequencies. This leads to a fast disappearance of the second term in equation (56), often referred to as the coherent term, while a slow decay governed by the first term, the incoherent term, persists at longer times. This *biexponential decay* was theoretically derived among others by Bixon and Jortner (1968) (see also Delory and Tric 1974, Lahmani *et al.* 1974, van der Werf and Kommandeur 1976) and has experimentally been observed in many molecules (cf. table 2). To exemplify this behaviour we may assume that the oscillator strength is equally distributed among all eigenstates, i.e. we use the egalitarian model (Lahmani *et al.* 1974)

$$|c_{sn}|^2=\frac{1}{N+1}, \qquad \gamma_n=\bar{\gamma}. \tag{59}$$

In this case the intensity equation (56) is expressed as

$$I(t)\sim(N+1)\exp(-\bar{\gamma}t)+\sum_{n\neq n'}\cos(\omega_n-\omega_{n'})t\exp(-\bar{\gamma}t). \tag{60}$$

At time $t=0$ we have

$$I(0)\sim(N+1)+N(N+1)=A^{\text{inc}}+A^{\text{coh}}, \tag{61}$$

representing the sum of incoherent and coherent contributions while for later times the coherent term has averaged out representing the nonradiative decay. The fraction

$$\frac{I(0)}{A^{\text{inc}}}=N+1, \tag{62}$$

yields the number of excited eigenstates for this simple model.

More realistic molecular models require numerical simulation studies to predict characteristic features of the time behaviour (Delory and Tric 1974, Chaiken *et al.*

Table 2. Some polyatomic molecules displaying singlet-triplet quantum beats and biexponential decay.

Molecule	References
Anthracene	Lambert *et al.* (1981) Zewail *et al.* (1982)
Biacetyl	van der Werf and Kommandeur (1976) Chaiken *et al.* (1979, 1981a) Henke *et al.* (1981)
Butynal	Mühlbach and Huber (1986) Bitto *et al.* (1989)
Glyoxal	van der Werf *et al.* (1975)
Methylglyoxal	Coveleskie and Yardley (1975, 1976) van der Werf *et al.* (1976) Chaiken *et al.* (1981a) Gurnick *et al.* (1981) Chaiken and McDonald (1982)
Propynal	Stafast *et al.* (1983) Bitto *et al.* (1984)
Pyrazine	Frad *et al.* (1974) ter Horst *et al.* (1981) Felker *et al.* (1982) van der Meer *et al.* (1982) Kommandeur *et al.* (1987) Kommandeur (1988)
Pyrimidine	Jameson *et al.* (1981) Okajima *et al.* (1982) Saigusa and Lim (1982)
Quinoxaline	McDonald and Brus (1974) Soep and Tramer (1975)
s-Triazine	Nott and Selinger (1978) Ohta and Baba (1981) Saigusa and Lim (1983)

1981b, Gurnick, *et al.* 1981, Khoo *et al.* 1983). While randomly distributed levels give rise to an unstructured slow decay component, correlated spectra, for which small beat frequencies are absent due to level repulsion, show a 'correlation hole' (Leviandier *et al.* 1986, Zimmermann *et al.* 1987). Such a depression in the fluorescence intensity right after the fast decay component has been detected by Bitto *et al.* (1989) and it demonstrates that level correlation can be directly observed in the time domain.

The number N of interacting background states can be related to the density ρ_t of triplet states. With increasing ρ_t the chance of finding interacting states in the vicinity of the excited singlet state increases. It is shown in figure 11 that with higher and higher vibrational excess energy ρ_t increases and the spectroscopic feature of the molecule turns, as expected, from small to intermediate (Mühlbach and Huber 1986).

Besides this unselective dependent of N on ρ_t the selection rules, governing intersystem crossing, depend on the excited state quantum numbers and symmetry. For this reason, N may show a strong, seemingly uncorrelated state-to-state

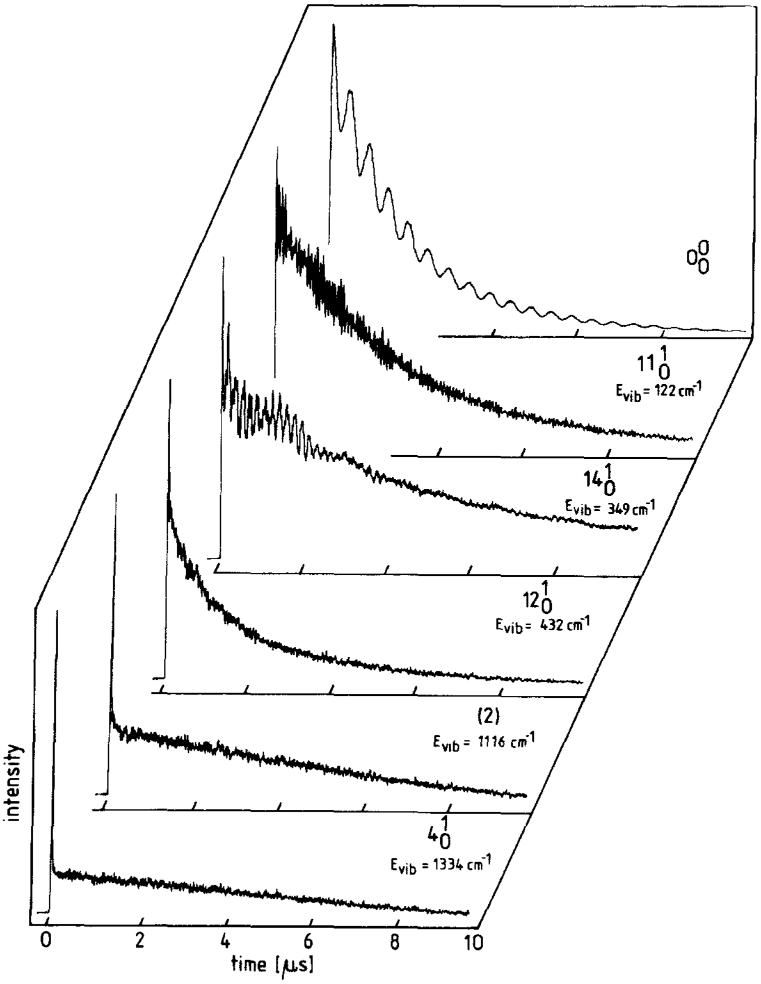
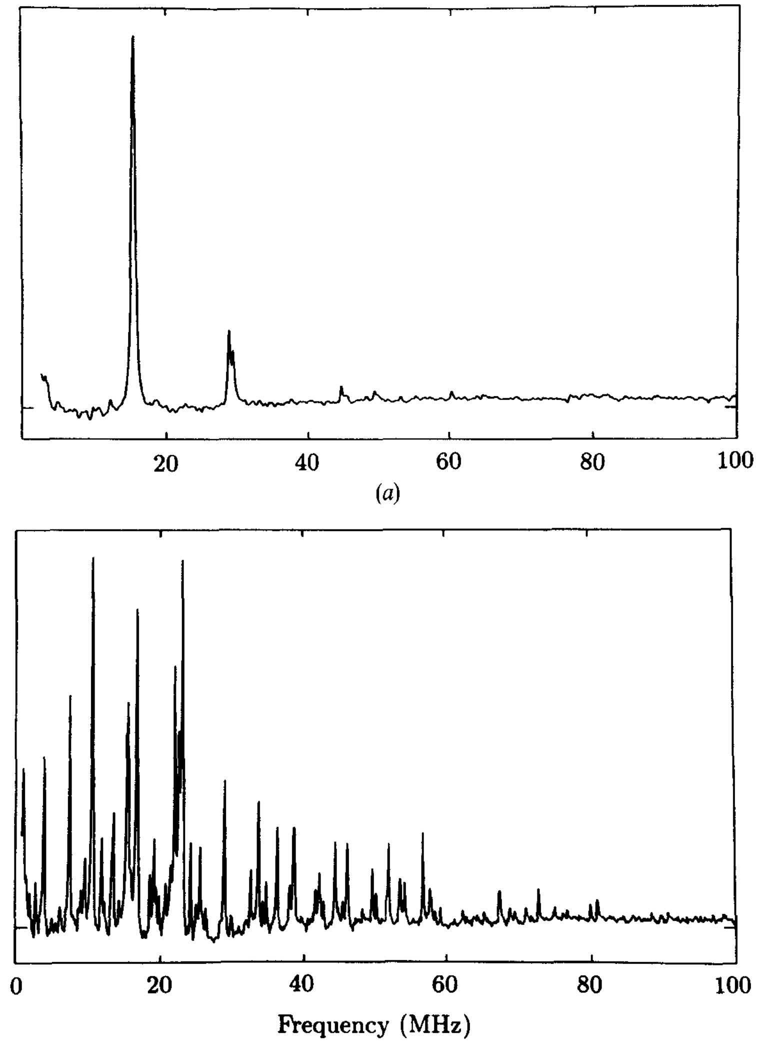


Figure 11. Time-resolved fluorescence decay curves of selected S_1 vibronic bands of butynal CH_3CCCHO. With increasing vibrational excess energy and thus with increasing state density ρ_t the distinct quantum beat structure evolves into a biexponential decay (Mühlbach and Huber 1986).

dependence on rotational quantum numbers (Watanabe *et al.* 1983b) or a linear correlation with J (ter Horst *et al.* 1981, Saigusa and Lim 1983, Matsumoto *et al.* 1983, Amirav and Jortner 1986). The evolution from a relatively low to a relatively high density of states may, therefore, occur over only a few J of rotational excitation indicating the break-down of simple selection rules. An instructive example of such a behaviour has recently been observed for propynal (Willmott *et al.* 1991) and is shown in figure 12.

4. Conclusions

Laser quantum beat spectroscopy is based on the superposition principle of quantum mechanics. A short laser pulse coherently excites the molecule into a superposition of energy eigenstates which are located within the coherent bandwidth of



(b)

Figure 12. Fourier spectra of quantum beat decays for two rotational states, $|2_{02}\rangle$ (*a*) and $|6_{24}\rangle$ (*b*), of a single vibronic band of propynal. The increase of the number of beat lines from a state with $J=2$ to one with $J=6$ illustrates the increase of the density of coupling states which is due to the break-down of the ΔK selection rule (Willmott *et al.* 1990).

the laser. The emissions of the different molecular eigenstates interfere and, consequently, the time-resolved total intensity is modulated at frequencies corresponding to the differences of the energy eigenvalues. According to this information a time-resolved spectroscopic technique becomes available that provides a high energy resolving power and a great versatility. The method is essentially Doppler-free since the radiation is emitted by single-particle sources and an energy resolution can be achieved which is limited only by the lifetime of the excited states.

The technique of monitoring the time-resolved evolution of well prepared superposition states by fluorescence detection or other means opens up the possibility to study the dynamics of excited molecular states very directly. The time evolution of the fluorescence, as shown above, mirrors intramolecular processes, which are expressed in terms of coupling strengths and level statistics, or intermolecular processes like collisional dephasing (Brucat and Zare 1984, Jeys *et al.* 1984). Thus, quantum beat spectroscopy as a method complementary to the frequency domain steady-state techniques is an indispensable tool in the study of excited molecular states with regard to both their spectroscopic nature in terms of structure parameters, and their dynamics. Moreover, the formalism developed in the treatment of quantum beats is readily extended to include state selective molecular behaviour and wave packet dynamics.

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