

tural, and functional models for the aforementioned adsorbate species. The reactivity of these ion pairs is strongly dependent upon the coordinative properties of the charge-compensating anion, in agreement with the support sensitivities seen in the heterogeneous systems. The most loosely connected ion pairs are extremely reactive, with catalytic activities approaching those of the supported catalysts. Moreover, the soluble group 4 complexes can serve as stoichiometrically precise models for several important classes of alumoxane-based olefin polymerization catalysts. These results

show that exciting opportunities exist where heterogeneous catalysis can teach us new things about homogeneous catalysis and vice versa. The challenge lies in building bridges between the two areas using the appropriate physicochemical techniques and synthetic strategies.

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## Molecular Quantum Beats. High-Resolution Spectroscopy in the Time Domain

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Chemistry is the world of molecules, and within this world the chemical reaction is one of the most important parts, if not the most important. How molecules decay and how they react with other molecules on a microscopic basis is of most interest to the chemist.<sup>1</sup> The understanding of chemical reactions requires, however, a very detailed knowledge of the molecular electronic structure, for even its smallest features can have a decisive influence on the dynamics of such complex systems as molecules. The exploration of the atomic and molecular electronic structure has benefited greatly from high-resolution spectroscopy, which has progressed considerably since the advent of the laser by taking advantage of the unique laser properties such as monochromaticity, high intensity, and extremely short pulses. The rapid development of the laser has produced state-of-the-art systems whose characteristics are close to the limits imposed by physical laws. With respect to the frequency domain, continuous-wave lasers nowadays feature bandwidths well below 1 kHz whereas, with respect to the time domain, pulses as short as 6 fs have been successfully generated. So it seems that narrow-band laser radiation should allow spectroscopists to resolve spectra of molecules in the gas phase to nearly any desired extent while the extremely short pulses may be used to reveal the dynamics of atomic motion in a molecule. This remarkable

radiation of "purest color" is available, and even this is tunable. However, it is not the light source that limits the resolution but the simple fact that the motion of the freely moving gas molecules causes line broadening in the spectra due to the Doppler effect.

Several spectroscopic methods have been developed to overcome Doppler broadening, for example, nonlinear techniques such as saturation spectroscopy, polarization spectroscopy, or two-photon spectroscopy with counterpropagating laser beams, as well as simple reduction of the molecules' velocity spread in molecular beams. Another method, conceptually very fundamental and experimentally relatively inexpensive, is based on the quantum beat phenomenon. Quantum beats appear as oscillations superimposed on the time-resolved fluorescence after a laser pulse has excited within its energy uncertainty two or more states in an atom or molecule. The frequencies of the quantum beats are just the energy differences between the "coherently" excited states.

This effect, lying at the heart of quantum mechanics, was introduced to atomic spectroscopy by Alexandrov and by Dodd and co-workers in 1964, but only with the introduction of the pulsed laser have quantum beats become interesting for a spectroscopic application.<sup>2</sup> It is the aim of this Account to give a short and simple description of just this phenomenon and to show how it is utilized as a high-resolution, molecular spectroscopic technique in the time domain, going far beyond rotational resolution.<sup>3-5</sup> The power and versatility of quantum beat spectroscopy will then be demonstrated

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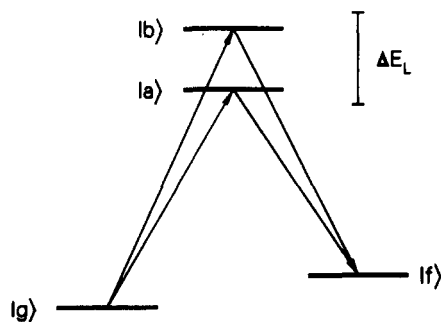
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**Figure 1.** Molecular four-level system, exhibiting quantum beats, i.e., interference in the time-resolved fluorescence of the coherently excited states  $|a\rangle$  and  $|b\rangle$ .

by using some instructive examples taken from our recent work. Since these experiments were carried out under isolated molecule conditions at low temperature in a gas beam, the effects of intermolecular relaxation processes are not discussed here. However, the method is not limited to the dilute gas phase. As has recently been demonstrated, quantum beats in the fluorescence can be observed in condensed matter, for instance, in semiconductors.<sup>6</sup>

Oscillating optical signals occur also in other fields of optical spectroscopy though they are of different physical origin and will not be discussed in this Account. We only mention briefly a few phenomena from which quantum beats should be distinguished. In optical coherence spectroscopy, oscillatory transients are observed such as optical nutation and optical free induction decay. They are invaluable for the determination of optical dephasing times  $T_1$  and  $T_2$  required for the investigation of intra- and intermolecular interactions. (For a review of coherence spectroscopy, the reader is referred to an earlier Account.<sup>7</sup>) A nonlinear method that may also exhibit beating signals is four-wave mixing,<sup>8</sup> one of the signals, coherent Raman scattering, gives rise to beating phenomena in direct time-resolved measurements<sup>9</sup> as well as in their interferometric variant.<sup>10</sup> Both techniques provide energy spacings of rotational and vibrational states in ground-state molecules.

### What Are Quantum Beats?

A quantum beat is a quantum mechanical interference effect that occurs in the time evolution of nonstationary states in atoms and molecules. Figure 1 shows a molecular four-level system with a ground or initial state  $|g\rangle$ , two closely spaced excited states  $|a\rangle$  and  $|b\rangle$ , and a final state  $|f\rangle$ . A photon from a short laser pulse with an energy uncertainty according to Heisenberg's energy-time uncertainty exceeding the spacing between  $|a\rangle$  and  $|b\rangle$  excites the molecule from state  $|g\rangle$  to either state  $|a\rangle$  or state  $|b\rangle$ . Following this excitation process the photon is reemitted, leaving the molecule in the final state  $|f\rangle$ . The photons or waves, to use the other picture, emitted from states  $|a\rangle$  or  $|b\rangle$  have a fixed phase relation, and consequently, a detector detects an interference pattern after a sufficient number of ab-

sorption-emission events have been collected.<sup>5</sup>

Obviously, the lack of knowledge as to which of the two states is excited, and hence, from which of the excited states the detector receives the photon, is the cause of the interference. To take these facts properly into account,<sup>4,5,11</sup> the state  $|\psi(t=0)\rangle$  prepared by the short pulse has to be expressed as a superposition (coherent) state:

$$|\psi(t=0)\rangle = c_a|a\rangle + c_b|b\rangle \quad (1)$$

Since  $|c_a|^2$  and  $|c_b|^2$  represent the probabilities of having excited states  $|a\rangle$  and  $|b\rangle$ , respectively, we may replace the coefficients  $c_a$  and  $c_b$  by the transition dipole matrix elements  $\mu_{ag} = \langle a|\mu|g\rangle$  and  $\mu_{bg} = \langle b|\mu|g\rangle$ , respectively, and rewrite eq 1 as

$$|\psi(t=0)\rangle \cong \mu_{ag}|a\rangle + \mu_{bg}|b\rangle \quad (2)$$

Let us now express the time evolution of this nonstationary state by assuming that the exciting laser pulse is much shorter than any relaxation process of  $|\psi\rangle$ . Under these conditions we simply have to introduce into eq 2 the respective Schrödinger phase factors:

$$|\psi(t)\rangle \cong \mu_{ag}e^{-iE_a/\hbar + \gamma_a/2)t}|a\rangle + \mu_{bg}e^{-iE_b/\hbar + \gamma_b/2)t}|b\rangle \quad (3)$$

where  $E_a$  and  $E_b$  are the energies of the states  $|a\rangle$  and  $|b\rangle$ , respectively, and the decay of the excited states, radiative or nonradiative, has been taken into account in a phenomenological way by introducing the decay constant  $\gamma_a$  for  $|a\rangle$  and  $\gamma_b$  for  $|b\rangle$ . Because the experiments are carried out in the gas phase under collisionless conditions, other relaxation processes are not relevant. Though various detection modes are possible, the time evolution of  $|\psi\rangle$  is most conveniently monitored via the fluorescence decay of the transition  $|\psi\rangle \rightarrow |f\rangle$ . The fluorescence intensity is then given by the expression

$$I_{ff}(t) \sim |\langle f|\mu|\psi(t)\rangle|^2 \quad (4)$$

which after inclusion of eq 3 and taking the modulus becomes

$$I_{ff}(t) \sim |\mu_{ag}|^2|\mu_{fa}|^2e^{-\gamma_a t} + |\mu_{bg}|^2|\mu_{fb}|^2e^{-\gamma_b t} + 2|\mu_{ag}\mu_{bg}\mu_{fa}\mu_{fb}|e^{-(\gamma_a+\gamma_b)t/2} \cos((E_b - E_a)t/\hbar) \quad (5)$$

where the matrix elements  $\langle f|\mu|i\rangle$  equal  $\mu_{fi}$ , with  $i = a, b$ .

This expression reveals quite clearly the features of a quantum beat signal: The first two terms represent the independent exponential decay of the eigenstates  $|a\rangle$  and  $|b\rangle$  while the third term, the cross or interference term, describes an exponentially damped oscillation of frequency  $\omega_{ba} = (E_b - E_a)/\hbar$ . This oscillation is called a quantum beat because the frequencies introduced by the quantum mechanical phase factors  $e^{-iE_a t/\hbar}$  and  $e^{-iE_b t/\hbar}$ , not being accessible to direct observation, are manifested as a beat at their frequency difference.

By passing from the "gray" theory to the "colorful" experiment we inspect Figure 2a. This emission decay, which was observed in the fluorescence of the molecule propynal, HC≡CCHO, exhibits two superimposed oscillations of similar frequencies.<sup>4</sup> When a Fourier transformation is applied in order to pass from the time domain into the frequency (i.e., energy) domain, the two

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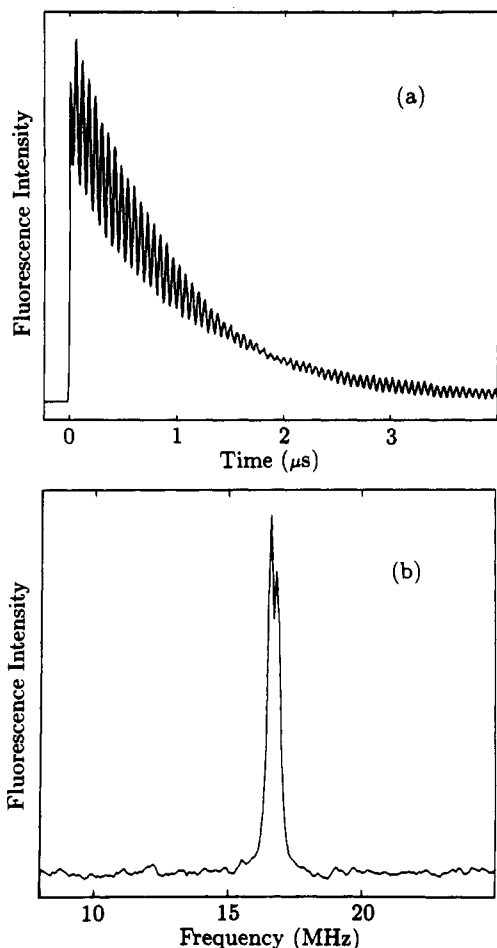
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**Figure 2.** Quantum beats in the fluorescence decay of  $S_1$  propynal demonstrating the high resolution of quantum beat spectroscopy. The fluorescence decay (a) has two superimposed oscillations as revealed in the real part of its Fourier transform (b).

beat frequencies are, as shown in Figure 2b, easily resolved although they are separated by only 200 kHz or  $7 \times 10^{-6} \text{ cm}^{-1}$ . This high resolution is achieved simply because the fluorescence lifetime is  $1 \mu\text{s}$ , which corresponds to a natural linewidth and, consequently, to a resolution of  $\sim 150 \text{ kHz}$ . The spectroscopic information extracted from this decay tells us that two sets of two levels have been coherently excited which are separated by 16.6 and 16.8 MHz. The energy separation of the two sets and their absolute ordering of the levels are, however, not obtained with the quantum beat method.

Before presenting examples on quantum beat spectroscopy, a summary is in order. Quantum beats are the effect of a single molecule and a single photon absorbed and then reemitted by two indistinguishable channels.<sup>2,5</sup> Consequently, in order to observe quantum beats an experimentalist must ensure that both channels remain indistinguishable during the measurement. Observing the fluorescence decay via a resolved transition, say  $|a\rangle \rightarrow |f\rangle$ , would, therefore, lead to a loss of the quantum beat, as blocking of one slit in the famous Young's double slit experiment would result in a loss of the fringes. Indistinguishable pathways with respect to spectroscopy means that all transition dipole moments of the eigenstates  $|a\rangle$  and  $|b\rangle$  to the ground states  $|g\rangle$  and  $|f\rangle$  are nonvanishing (see eq 5) and that the beat modulation is deepest when the two absorption and the two emission transition dipoles are equal ( $\mu_{ag} = \mu_{bg}$ ;  $\mu_{af}$

$= \mu_{bf}$ ). Note also that each elementary absorption-emission process has to start and to end at single ground states (see Figure 1).

This simple description already shows the strength of the quantum beat phenomenon when applied to molecular spectroscopy. It provides (i) essentially Doppler-free spectroscopy, (ii) high-energy resolution that is limited only by the lifetime of the coherently excited states, and (iii) spectroscopy that is insensitive to saturation effects. Finally, the method is fundamental, simple, direct, and sensitive.

### How Quantum Beats Are Measured

Spectra of polyatomic molecules measured at room temperature are often congested because a large number of quantum states of the rotational and vibrational degrees of freedom are thermally populated. As a consequence, many transitions are pumped simultaneously and, due to the optical selection rules, many of the excited states are not excited coherently, initially resulting in a mixture of incoherent and coherent states. Because incoherently excited states contribute only to the nonmodulated fluorescence; the relative modulation depth of the quantum beats is reduced to such a degree that quantum beat measurements are not feasible. The selectivity of the excitation process and hence the relative intensity of the beat amplitude are, however, greatly increased by cooling the molecules to low temperatures and by using narrow-band laser pulses. With supersonic jet expansion seeded in a noble gas the molecules are conveniently and effectively cooled to a rotational temperature of a few kelvins, and as a further benefit, molecular collisions during the time evolution of the superposition state are avoided.

Commercially available dye lasers deliver tunable radiation of 1–2-GHz bandwidth in pulses of  $\sim 5 \text{ ns}$  which is suitable for selective excitation of single rotational states in small polyatomic molecules. This bandwidth is adequate for most of the quantum beat experiments described in this Account, although it does not provide the ultimately achievable resolution of, for example, 88 MHz (fwhm) given by a 5-ns (fwhm) Fourier transform limited (FTL) pulse with a Gaussian profile. Such pulses are, however, required for highest resolution experiments.<sup>12</sup>

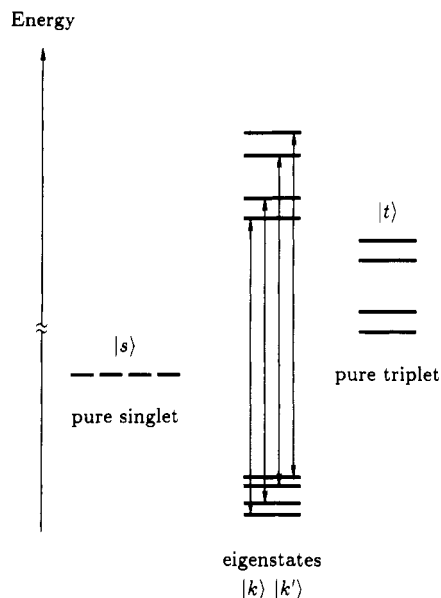
If quantum beats are monitored by emission, the detection system consists of a photomultiplier tube that is connected to a transient digitizer or a digital storage oscilloscope. For the detection of isotropic quantum beats the total undispersed emission is imaged onto the photomultiplier, whereas for anisotropic quantum beats a polarizer is added to detect the appropriate polarization component of the emission. Owing to the high resolution in quantum beat spectroscopy, meaningful spectroscopic measurements are in most cases obtained only when the Earth's magnetic field is carefully compensated in order to avoid undesired Zeeman splitting.

### Molecular Quantum Beats

In the early days of the theory of radiationless transitions, it was predicted that quantum beats should be observed following coherent excitation of molecular eigenstates.<sup>13</sup> This prediction drew much debate in the

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**Figure 3.** Level diagram of singlet-triplet interaction in the presence of hyperfine interaction. In propynal each rovibronic state is split into four hyperfine states, which gives rise to four quantum beats.

physical chemistry community until quantum beats were finally detected by McDonald and co-workers in the fluorescence of biacetyl<sup>3</sup> (for further references, see ref 14).

In electronically excited states of polyatomic molecules, spin-orbit interaction is appreciable so that the states are properly described as mixtures between a pure singlet state  $|s\rangle$  and a pure triplet state  $|t\rangle$  according to

$$|k\rangle = c_{sk}|s\rangle + c_{tk}|t\rangle \quad \text{and} \quad |k'\rangle = c_{s'k'}|s\rangle + c_{t'k'}|t\rangle \quad (6)$$

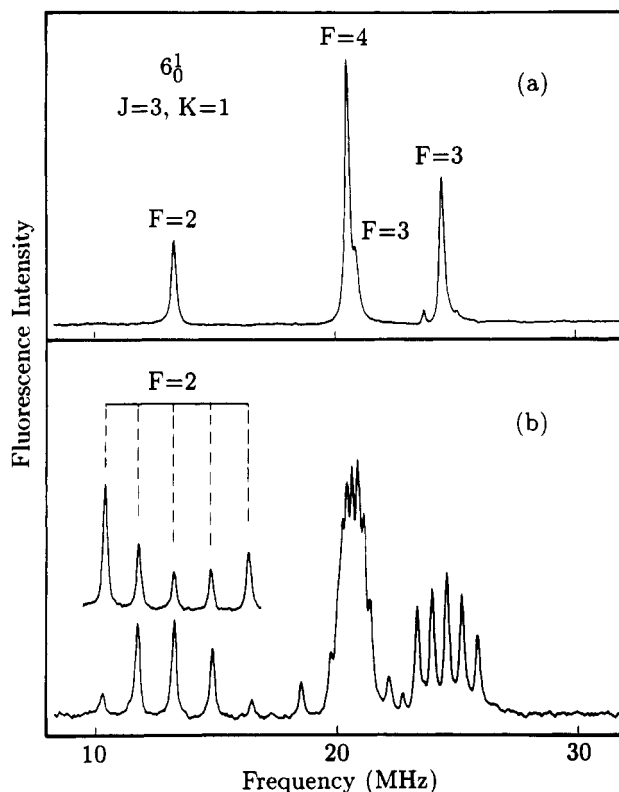
The pure states  $|s\rangle$  and  $|t\rangle$  are often referred to as Born-Oppenheimer (BO) states and  $|k\rangle$  and  $|k'\rangle$  as eigenstates of the molecular Hamiltonian  $H_{\text{MOL}} = H_{\text{BO}} + H_{\text{SO}}$ , with  $H_{\text{SO}}$  describing the spin-orbit interaction.<sup>15</sup> The energy spacing of the two eigenstates expressed in terms of the energy difference of the BO states  $\Delta E_{st}$  and the spin-orbit matrix element  $v_{st}$  is<sup>15</sup>

$$\hbar\omega_{kk'} = (\Delta E_{st}^2 + 4|v_{st}|^2)^{1/2} \quad (7)$$

where  $\omega_{kk'}$  is the quantum beat frequency observed upon coherent excitation of the eigenstates. The time-resolved fluorescence  $I_n(t)$  of this two-level system is given by eq 5. The analysis of the emission decay<sup>15</sup> provides not only the energy difference of the two eigenstates by the measured beat frequency  $\omega_{kk'}$  but also the spin-orbit coupling strength  $v_{st}$  by the modulation depth and the extent of the singlet-triplet mixing in terms of the coefficients of eq 6.

### Resolving and Identifying Hyperfine Structure

The resolving power of the quantum beat method reveals, however, much more structural detail. If the molecule possesses nuclei with a nuclear magnetic moment, then the interaction of the electron and nuclear spins gives rise to hyperfine structure as illustrated by



**Figure 4.** Fourier spectra of hyperfine quantum beats observed (a) in zero field and (b) in a magnetic field of  $B = 1.5$  G. Changing the laser polarization from  $\epsilon^L \parallel B$  to  $\epsilon^L \perp B$  (inset of part b) provides a characteristic change of the intensity pattern of the Zeeman components for each zero-field quantum beat frequency.

the level diagram in Figure 3.<sup>16</sup> In the case of propynal the two nonequivalent protons with nuclear spins  $I_1 = 1/2\hbar$  and  $I_2 = 1/2\hbar$  split each rotational state into four hyperfine states of total angular momentum  $F = J + I_1 + I_2$ . Hence, a laser pulse that coherently excites the four pairs of eigenstates creates, in accordance with the selection rules, the four quantum beats indicated in Figure 3. The experimental result of a rotational state of  $J = 3$  is shown in Figure 4a; it was obtained by carefully compensating for the Earth's magnetic field.

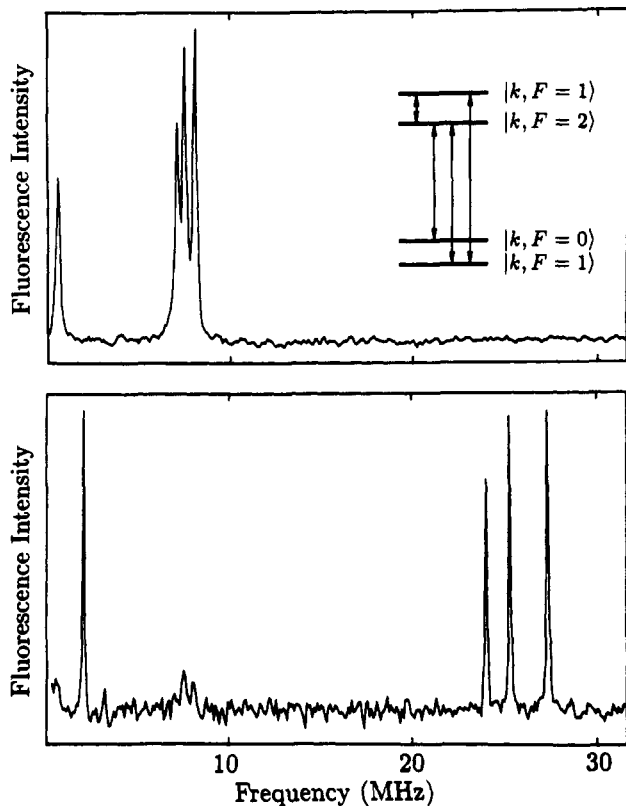
Identification of these hyperfine states is accomplished by making use of the Zeeman effect. A small magnetic field of about 1.5 G, merely 3 times that of the Earth, splits the eigenstates into  $2F + 1$  Zeeman components, which gives rise to  $2F + 1$  quantum beats for each beat previously observed in zero field as shown in the Fourier spectrum (Figure 4b). In the case of congested Zeeman spectra, selective variation of the laser polarization with respect to the magnetic field axis can be very helpful for the assignment because the intensity patterns of the Zeeman components change in a very characteristic way. On the basis of such a procedure the quantum numbers  $F = 2, 3, 3, 4$  were unambiguously assigned.<sup>15</sup>

In addition to the quantum beats between the  $|k, F\rangle$  and the  $|k', F\rangle$  states, which are subject to the selection rule  $\Delta F = 0$ , there are also coherences among the hyperfine levels of either the  $|k\rangle$  or the  $|k'\rangle$  state as indicated in the inset of Figure 5. These beats are denoted as hyperfine polarization quantum beats because,

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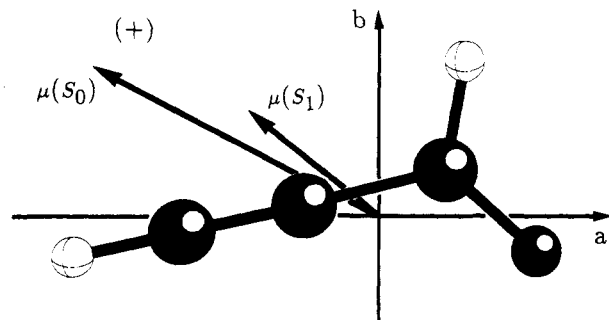


**Figure 5.** Quantum beats among hyperfine levels of eigenstates  $|k, F\rangle$  (top) and  $|k', F\rangle$  (bottom). The observed frequencies arise due to coherences indicated in the inset in the top panel as opposed to those sketched in Figure 3. Excitation of the eigenstates  $|k', F\rangle$  with predominant triplet character (bottom) and, therefore, with the greater hyperfine splittings exhibits the greater frequencies.

occurring between different  $F$  states, the emission is anisotropic in space.<sup>4,5,12</sup> Therefore, they are easily distinguished from the former isotropic beats with polarized excitation and detection. If a large spin-orbit splitting allows selective excitation of either the  $|k, F\rangle$  or the  $|k', F\rangle$  hyperfine level set, we observe a particularly simple quantum beat pattern. The results of such a case are shown in Figure 5, where the upper panel displays the beat frequencies from the eigenstate  $|k\rangle$  with mainly singlet character, while the lower panel displays those from  $|k'\rangle$ , which has primarily triplet character and thus a larger "content" of magnetic moment resulting in greater hyperfine splittings. The analysis of these spectra provides a deep insight into the electronic structure of the molecule such as the electronic spin density distribution by means of Fermi contact and dipole-dipole constants as well as the role played by hyperfine interaction in the molecular relaxation process.<sup>12,17</sup>

### Quantum Beats in an External Electric Field

The permanent electric dipole moment  $\mu$  of a molecule is of importance for the determination of the electronic charge distribution as well as for an assessment of the interaction among molecules. For the measurement of  $\mu$  the Stark effect has been most helpful.<sup>16</sup> Placing a molecule with a permanent electric dipole into an electric field  $\mathcal{E}$  influences the rotational



**Figure 6.** Electric dipole moment of the  $S_0$  and the  $S_1$  electronic states ( $v = 0$ ) of propynal. They are given with respect to the principal axes of inertia. (Propynal is depicted in the  $S_0$ -state geometry.)

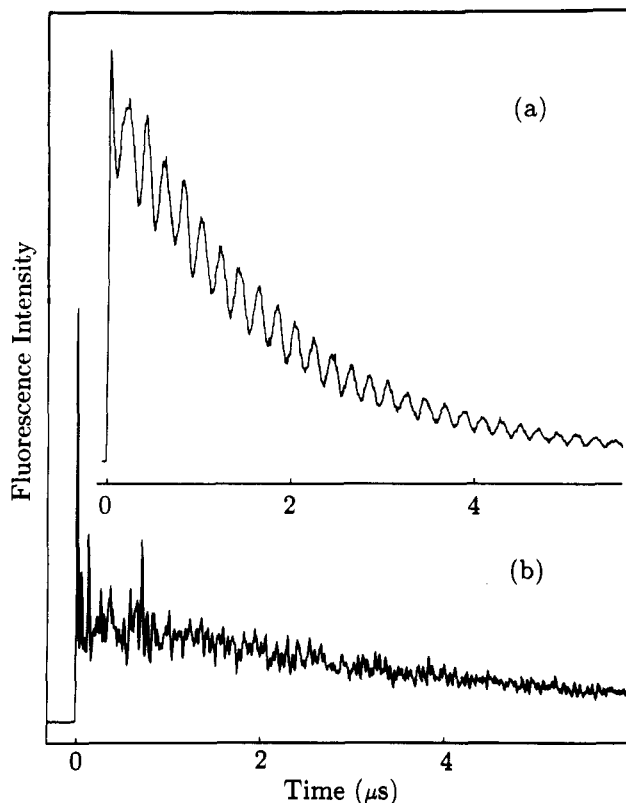
motion of the molecule, which results in a shift of the rotational energy levels (Stark tuning). Furthermore, a splitting into sublevels is observed; more specifically, a rotational state with angular momentum  $J$  is split into the  $2J + 1$  Zeeman sublevels.<sup>16</sup> When such a sublevel structure is excited by a properly polarized laser pulse ( $\epsilon^L \perp \mathcal{E}$ ) and one linearly polarized component of the fluorescence is selectively detected ( $\epsilon^D \perp \mathcal{E}$ ), quantum beats can be observed.<sup>18</sup>

Stark quantum beats have been employed to measure dipole moments of molecules in electronically excited states.<sup>4,18</sup> If the dipole vector coincides with one principal axis of inertia as in diatomic molecules or in molecules with sufficiently high symmetry, its absolute value is simply determined by choosing a convenient, single rotational state for the measurement of the Stark splitting as a function of the field strength. In the case where the dipole moment has components along two or three axes of inertia, the Stark tuning of individual rotational states depends on a different extent on the dipole components and, consequently, a set of at least as many states as there are nonvanishing components has to be considered. Such measurements give us the possibility of determining the magnitude and orientation of the dipole vector in a polyatomic molecule.

Full determination of an excited-state dipole moment by the Stark quantum beat technique has recently been demonstrated for propynal in the  $S_1$  state.<sup>18</sup> Conventional Doppler-limited Stark spectroscopy merely provides the component  $\mu_a$  of this near-prolate asymmetric rotor molecule, because at the high field strengths required to obtain Stark splittings exceeding the Doppler width, only the linear Stark effect can be measured. The Doppler-free Stark quantum beat method, working at very low field strengths, provides an accuracy which in the case of propynal has been shown to be comparable with microwave spectroscopic measurements of the ground-state dipole moment. Comparison of the  $S_1$  dipole moment ( $|\mu| = 1.37$  D,  $\mu_a = -0.874$  D,  $\mu_b = 1.06$  D) with the  $S_0$  moment ( $|\mu| = 2.78$  D,  $\mu_a = -2.36$  D,  $\mu_b = 1.47$  D) shows the effect of electronic excitation on the dipole moment as portrayed in Figure 6. Its magnitude is reduced by a factor of 2, and the vector is rotated toward the  $b$  axis such that it is almost parallel to the CO bond. This is a consequence of electron transfer and delocalization upon the  $n\pi^*$  excitation, in which an electron is transferred from the nonbonding

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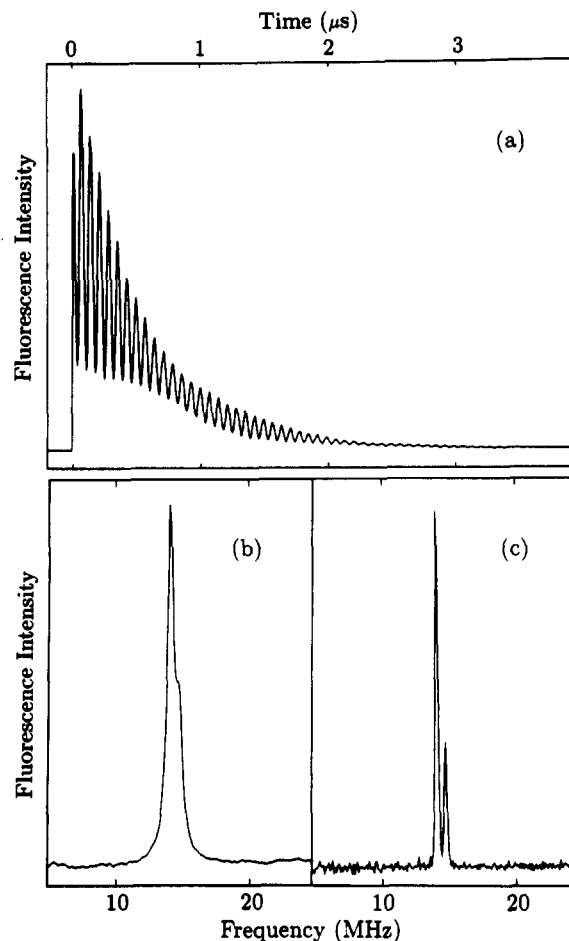
**Figure 7.** Quantum beats in the  $S_1$  state of butynal. The fluorescence decays observed in the vibrationless state (a) and at vibrational excess energy of  $1330\text{ cm}^{-1}$  (b) demonstrate the effect of an increasing state density on the decay dynamics.

orbital at the oxygen atom to the  $\pi^*$  orbital of the CO bond.

### The Beat Goes On...

In the examples presented herein, quantum beat spectroscopy was applied for purely spectroscopic purposes. It was used for the spectroscopist's goal to determine molecular structural parameters and constants such as spin-orbit coupling matrix elements, hyperfine interaction constants, or electric dipole moments. Other constants have also been determined, though not discussed here, among which are Landé  $g$  factors,<sup>19</sup> rotational constants, and asymmetry splittings as well as vibrational frequencies and anharmonicities.<sup>18,20</sup> In this context we particularly refer to the work of Felker, Zewail, and co-workers, who applied coherences between rotational states to determine rotational constants and the geometry of large molecules and of complexes, the conventional spectra of which lack resolved rotational structure.<sup>14,21</sup>

On the other hand, quantum beat spectroscopy as a time-resolved technique can be an invaluable tool for investigating the dynamics of photophysical processes highlighted by studies of intramolecular vibrational energy redistribution in large molecules using picosecond pulses.<sup>14</sup> Extension of this work to the femtosecond region opened the spectacular world of real time probing of chemical reactions and spectroscopy of the transition state.<sup>22</sup> At first glance the connection to



**Figure 8.** Example of subnatural linewidth resolution. Fourier transformation of the full fluorescence decay (a) results in natural linewidth resolution in the Fourier spectrum (b). Biasing the long-lived fluorescence by multiplying the decay shown in part a with a Gaussian function (fwhm  $4.2\ \mu\text{s}$ , maximum at  $5.3\ \mu\text{s}$ ) improves the resolution by a factor of 2.5 in part c.

quantum beats may not be obvious, but the wavepackets prepared on excited-state potential energy surfaces by femtosecond laser pulses constitute a coherent superposition of vibrational (and continuum) states, the time evolution of which gives rise to quantum beats.<sup>22</sup>

In our work we used the high energy resolving power of quantum beat spectroscopy on the microsecond time scale to study the dynamics of small polyatomics, where eigenstates are coherently excited which are the result of the coupling of an emitting state (e.g., a BO singlet state) to a manifold of dark states (e.g., BO triplet states).<sup>4,5</sup> The quantum beat signal generalized to the case of  $N$  coherently excited eigenstates shows a total of  $N(N - 1)/2$  beat frequencies like the number of handshakes among  $N$  people. Analyzing such quantum beat decays by counting the number of quantum beat frequencies in the Fourier spectrum provides a powerful method for estimating the number of coherently excited states within the laser bandwidth and thus the state density.<sup>17,23</sup>

The dependence of the time-resolved fluorescence on the triplet-state density with increasing  $S_1$  vibronic

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excess energy in butynal,  $\text{H}_3\text{CC}\equiv\text{CCHO}$ , illustrates the transition from simple quantum beat decays to biexponential fluorescence decays as depicted in Figure 7. The fast decay component in part b originates from a large number of quantum beats, prepared in phase at the incidence of the laser pulse, but shortly after they interfere destructively. As some oscillations come back into phase at a later time, recurrence spikes appear superimposed on the slow decay component.<sup>23</sup> Investigation along this line, in particular in view of the level statistics and the dynamics in molecules, are in progress.

In our conclusion, we should reevaluate the resolving power of quantum beat spectroscopy. Lifetimes of 1–10  $\mu\text{s}$  provide a resolution of 150–15 kHz, which in conventional spectroscopy may prove difficult to achieve, but can be readily obtained in quantum beat spectroscopy regardless of the laser bandwidth. From the experimental point of view, it is the total observation time that limits the resolution. However, the resolution may be improved even beyond the natural linewidth if the emission of the *ensemble* of the excited molecules is biased in favor of the long-lived species in the data analysis.<sup>24</sup> The gain in resolution, as shown in the

example in Figure 8, is in accordance with Heisenberg's uncertainty principle because the natural linewidth is valid only for a nonselected ensemble of excited molecules decaying by spontaneous emission.

Clearly, quantum beat spectroscopy on the nano- and microsecond time scales is used advantageously whenever transitions should be resolved within the Doppler profile of a conventional spectrum. On the other hand, high temporal resolution, i.e., short pulse duration and short sampling intervals, allows us to detect high frequencies. Quantum beat frequencies exceeding the Doppler width can be observed with pico- or femtosecond resolution, but the corresponding energy differences are resolvable with less experimental effort by conventional spectroscopic methods. Thus, for high resolution in the energy domain, be slow, wait long enough, and use quantum beats...!

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## Orbital Stereochemistry: Discovering the Symmetries of Collision Processes

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### Introduction

One of the most exciting recent aspects of laser chemistry is the ability to prepare highly aligned, or directional, reagents using the polarization of lasers.<sup>1-5</sup> It is now possible to investigate chemical processes with directional control in a variety of new measurements. The results provide a means of visualizing the important symmetries of the chemical process with unprecedented detail. Many mechanistic interpretations of chemical transformations are built upon compelling pictures of orbital directionality, electron overlap and transfer, and symmetry arguments.<sup>6</sup> Chemists can exploit the methods of directional control to verify these pictures and to broaden our understanding of chemical stereospecificity.

Consider, for example, a simple case of a p orbital, which can be prepared with a laser from a ground s state and aligned along the direction of polarization of the light. The p orbital may be aligned parallel or

perpendicular to an oncoming collision partner by using well-defined crossed beams of reagents and by arranging the polarization of the excited light in the desired direction with respect to the relative velocity of approach (Figure 1). If a hypothetical chemical reaction requires the orbital to approach preferentially in the perpendicular direction in order to produce a favorable electron overlap, then a larger rate coefficient might be observed for the initial perpendicular orbital configuration than for the parallel preparation of the p state. With an appropriate mathematical formalism, it can be shown that the rate coefficient will increase and decrease smoothly with the form of a  $\cos(2\beta)$  function, repeating every  $180^\circ$  when the direction of the p orbital is rotated. Here  $\beta$  is the angle between the direction that the orbital lobes make with the relative velocity vector, as shown in Figure 1. The result gives a direct determination of the relevant orbital stereochemistry that is required for the reaction, i.e., an orbital alignment effect.

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