## 9. Two-level system in a laser field

### 9.1. Optical dynamics in the laser field

For the discussion of the ZPL of the pure electronic 0-0 transition, we can forget about vibrations and phonons. We consider our molecule as a two-level system, coupled on the one hand to the exciting laser field, and on the other hand to baths causing relaxation:

i) the empty photon modes responsible for spontaneous emission;

ii) the (usually thermally populated) bath of phonons and low-frequency degrees of freedom responsible for coherence loss, i. e., for the decoherence time (often called pure dephasing time in the earlier literature).

This problem is perfectly analogous to that of a spin-1/2 in a static magnetic field (the optical excitation frequency replaces the Zeeman splitting), submitted to an oscillating electromagnetic wave (the laser field replaces the radiowave or microwave used to achieve the magnetic resonance for a spin-1/2 in NMR or ESR). This analogy can be demonstrated rigorously from a density-matrix description of the two-level system (Feynman , Vernon, Hellwarth). Here, we just use the analogy with magnetic resonance with the following correspondence:

static field Zeeman splitting $\Leftrightarrow$ electronic transition energy

oscillating micro- or radio-wave $\Leftrightarrow$ laser wave

longitudinal magnetization $\Leftrightarrow$ population of excited state

transverse magnetization $\Leftrightarrow$ oscillating dipole moment of molecule.

Just as in magnetic resonance, the state of the two-level system can be represented as the Bloch vector, a vector restricted to the Bloch sphere (see Fig. 9.1). The population difference between ground and excited state, and the real and imaginary parts of the coherence (i.e., the off-diagonal element of the density matrix) can be seen as the three components of a 3-dimensional vector in a fictitious space, the Bloch vector (see Fig.9.1). If there is no relaxation, the Bloch vector remains on the sphere, because it is only subject to rotations. There are two possible components of the rotation vector in the rotating frame (in magnetic resonance, the reference frame rotating along the static magnetic field at the angular frequency of the oscillating magnetic field):

i) a rotation around the vertical axis (Fig. 9.2a), at a rate given by the detuning $\delta$ between the laser frequency $\omega$ and the resonance frequency $\omega_{eg}$ of the molecule,

$$\delta = \omega - \omega_{eg}$$

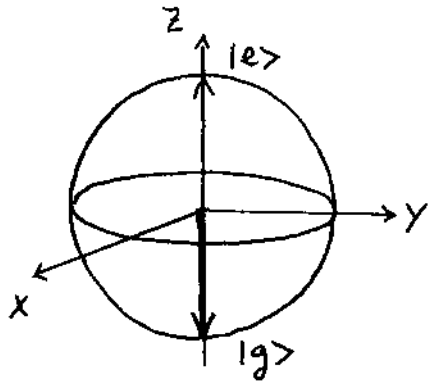


*Figure 9.1: The Bloch sphere, a convenient way to represent the state and the dynamics of a two-level system subject to a laser field.*

ii) a rotation around a horizontal axis (Fig. 9.2b) at a rate given by the Rabi frequency $\Omega$, proportional to the laser electric field $\vec{E}_0$ and to the transition dipole moment $\vec{\mu}_{eg}$ of the molecule :

$$\Omega = \left| \frac{\vec{\mu}_{eg} \cdot \vec{E}_0}{\hbar} \right|$$

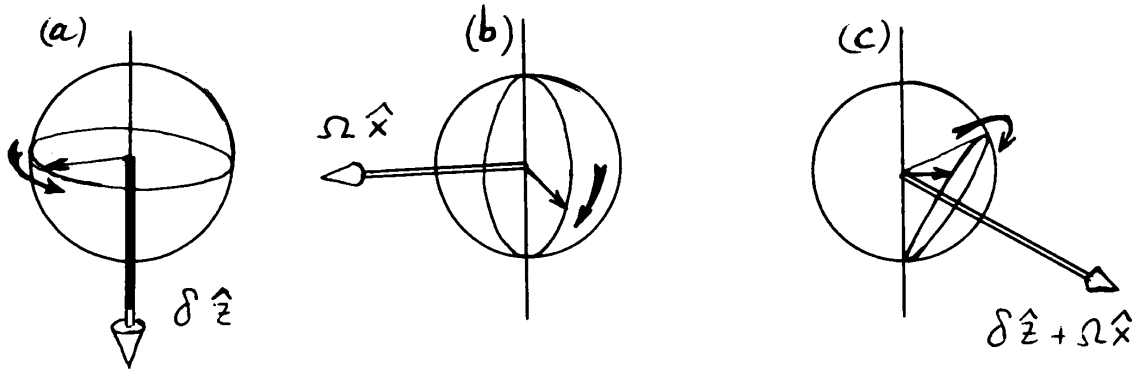


*Figure 9.2: A few cases of the rotation motion of the Bloch vector (thin line) around an effective rotation vector (or magnetic field in magnetic resonance), having the laser detuning as its vertical component, and the Rabi frequency (proportional to the laser field) as its horizontal component.*

The ground state corresponds to the lowest point of the sphere, the excited state to the highest point. The points on the vertical axis represent statistical mixtures of ground

and excited states, and the points on the ($X$,$Y$) equator circle represent *coherent* states with equal admixtures of ground and excited states.

We can now visualize the movement of the Bloch vector in the absence of relaxation, for the free evolution, without laser field (Fig. 9.2a), with a resonant laser (Fig. 9.2b), or in the general case of excitation with a non-resonant laser (Fig. 9.2c).

## 9.2. Relaxation and dephasing ; Bloch equations

Coupling a two-level molecule to a bath leads to two qualitatively different processes :

i) Non-adiabatic processes, in which the bath exchanges energy with the system. The bath must act via fluctuations at the transition frequency, i.e., at very high frequencies. In the case of optical transitions, the only process is population relaxation from the excited to the ground state. This relaxation can occur via spontaneous emission, or via non-radiative relaxation, in which the electronic energy is transformed into heat (usually into high-frequency vibrational modes of the molecule). For optical transitions, the population relaxation rate is usually nearly independent of temperature, of the matrix, or of the insertion sites.

ii) Adiabatic processes, in which the bath slightly changes the transition energy between the two levels, but does not induce transitions between the levels. In that case, the bath acts via its low-frequency fluctuations. This frequency is so low, that it is in general a good approximation to use a classical model for the bath (i.e., a model in which bath fluctuations are treated classically). The slight fluctuations of the transition frequency under bath fluctuations lead to a loss of memory of the phase, i.e., to a damping of the Bloch oscillation, and therefore to a broadening of the optical line. This is the origin of the decoherence (or pure dephasing) contribution to the homogeneous width.

The major cause of adiabatic relaxation for molecules in solids is coupling to the phonons, mainly the acoustic phonons which are still populated at low temperatures, and the low-frequency optical phonons, which are strongly coupled to the optical transition.

The Bloch relaxation times in the optical case are quite similar to those defined for the magnetization:

The relaxation time $T_1$ is the excited state lifetime (analogue of the magnetic longitudinal relaxation time). It describes how fast the population relaxes to equilibrium, in this case to the ground state. In general, contrary to magnetic resonance, there is no relaxation for the ground state in optical two-level systems (the temperature is much lower than the optical transition energy).

The relaxation time $T_2$ is the coherence lifetime (analogue of the magnetic transverse relaxation time). It is the inverse of the homogeneous width. As we have seen earlier,

$$\frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_2^*}$$

where $T_2^*$ represents the inverse of the rate of decoherence (or pure dephasing), due to adiabatic processes.

If we now introduce relaxation into the dynamics of the Bloch vector, we find, in addition to the coherent evolution caused by the laser field, two new processes. The Bloch vector relaxes at the dephasing rate $T_2^{-1}$ towards the vertical axis of the sphere. In addition, it also relaxes towards the ground state, i.e., the lowest point of the sphere, at a rate $T_1^{-1}$. When relaxation is present, the oscillating or rotating movements of the Bloch vector are damped. The Bloch vector relaxes towards the steady-state solution, which is constant in the rotating frame. The differential equations describing the movement of the Bloch vector under the coherent field and with relaxation are called Bloch equations. We won't write them explicitly in this course.

## 9.3. Optical saturation

We first qualitatively discuss the steady-state solutions of the optical Bloch equations. This steady state is reached in the frame rotating at the frequency of the laser oscillation. This means that the laser induces a forced oscillation of the system (the system accompanies the laser oscillation with a phase shift and an amplitude which vary according to the laser frequency). The steady state is reached when the variations of the Bloch vector due to relaxation are compensated by the variations due to

precession in the laser field. For example, in the case of a resonant laser field, the steady-state solution deviates from the ground state, which means that some coherence is established by the laser.

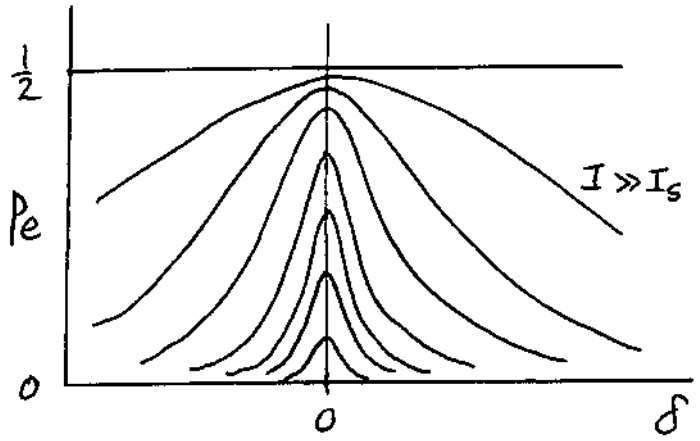


*Figure 9.3: Variations of the population of the excited state as a function of laser detuning for different laser powers, showing optical saturation and broadening of the resonance line.*

The vertical component of the Bloch vector gives the excited state population, which is proportional to the fluorescence intensity. This population is sketched in Figure 9.3 as a function of laser frequency, for various laser intensities. The response of the system at low intensity is linear, then it starts to saturate. This optical saturation manifests itself by the limitation of the fluorescence or absorption, and by the broadening of the optical line. At high power, it is possible to saturate the system with a non-resonant laser. This phenomenon is also called power broadening.

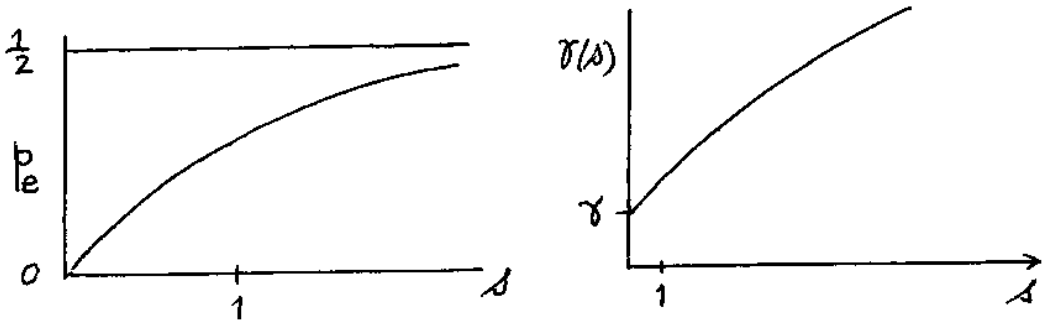


*Figure 9.4: Saturation of the population of the excited state for increasing laser intensity (normalized to saturation intensity), and power broadening of the line. The broadening increases as the square root of the intensity for large intensities. The laser excites all resonant molecules within the Rabi frequency, which is proportional to the laser field, i.e., to the square root of the intensity.*

The ratio of the laser intensity to the saturation intensity is called the saturation parameter $s$. The excited state population $p_e$ (proportional to the fluorescence intensity) and the saturated width $\Gamma(s)$ are given by:

$$s = \frac{I}{I_{sat}}; \quad p_e = \frac{1}{2}\frac{s}{1+s} \quad ; \quad \Gamma(s) = \Gamma(0)\sqrt{1+s} \quad . \qquad [9.1]$$

Figure 9.4 shows how the signal and the width depend on the laser intensity. Optical saturation had been observed long ago on the very sharp optical lines of atoms. For molecules in the solid state, such experimental observations were difficult because of the broad inhomogeneous profile. One could in principle observe saturation via spectral hole-burning, but many other sources of saturation (for example the saturation due to the photochemical hole-burning process) mask the optical saturation of the two-level system. Single-molecule observations, on the contrary, do not suffer from chemical saturation effects, and directly display optical saturation. Figure 9.5 shows an example of fluorescence excitation lines of a single dibenzoterrylene molecule in a naphthalene crystal at various laser powers.

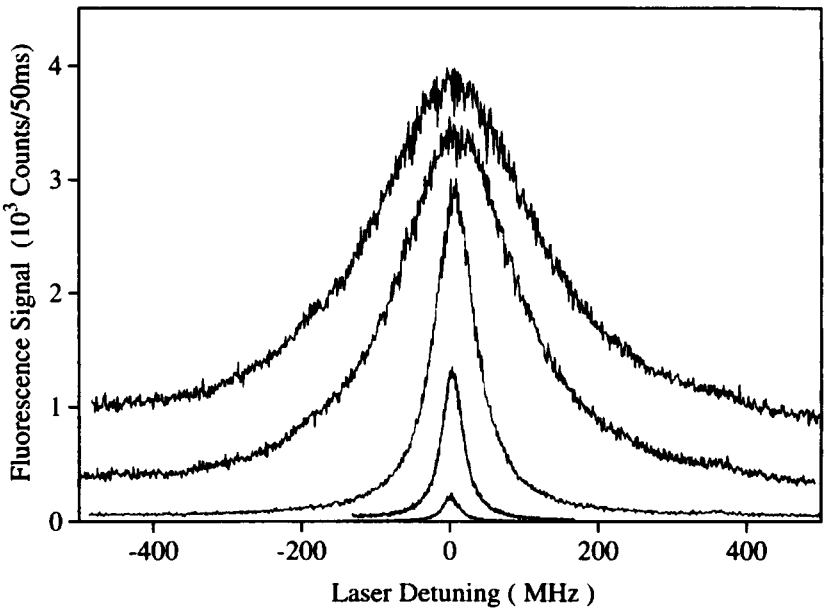


*Figure 9.5 : Saturation of the fluorescence excitation line of a single dibenzoterrylene molecule in a naphthalene crystal. The excitation intensity is increased by a factor 3-5 between each spectrum.*

## 9.4. Optical nutation

The dynamics of an optical two-level system in a quickly varying laser field can often be discussed qualitatively by means of the Bloch vector picture. We examine an important example of a transient solution of the Bloch equations, optical nutation. A constant field amplitude is suddenly applied at time zero. The system goes from the ground state at time zero (before the field was applied), to the steady state under constant illumination at long times. In the rotating frame, the system starts from a downward pointing Bloch vector (ground state) and starts to precess (or nutate) on a cone around the axis defined by the effective magnetic field $\vec{\tilde{\Omega}}$ resulting from the laser detuning (vertical component) and the laser field amplitude (Rabi frequency, transverse component). If no damping is present, the precession continues at the same rate as long as the laser field remains constant. If damping is present, the transient motion is damped with a characteristic time depending on the Rabi frequency and on the times $T_1$ and $T_2$ (see Figure 9.6), and the Bloch vector tends towards the steady-state vector.

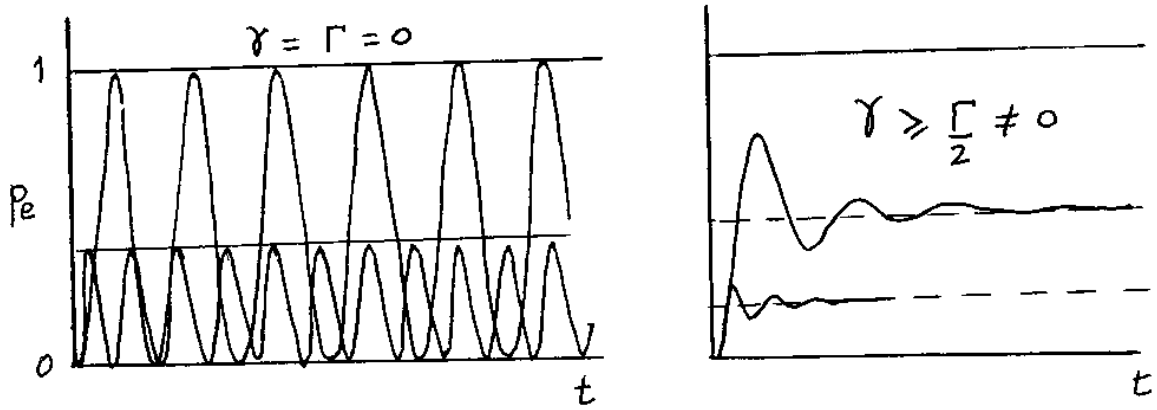


*Figure 9.6: Optical nutation of the Bloch vector when a constant laser field is established suddenly. The left-hand part of the figure shows Bloch oscillations in the absence of relaxation for resonant and non-resonant cases.. In practice, relaxation quickly damps the oscillations, leading to the characteristic nutation transients of the right-hand part.*

A very direct way to observe this transient motion is to select a single optical two-level system, e.g. a single molecule. The measured quantity is fluorescence, which is proportional to the population of the excited state. Because each observation of a photon means that the molecule has just reached the ground state, the observation projects the molecule into the ground state (in the quantum-mechanical sense). Therefore, the system starts from the ground state after each photon has been

detected, which is exactly the same problem as suddenly applying a constant laser intensity to a system previously in the ground state. Thus the probability per unit time of observing the next photon (after each photon observation) gives us the population of the excited state with the ground state as initial state. The histogram of time delays between consecutive photons is a picture of the time evolution of the excited state population during the optical nutation. As we discussed earlier, this histogram cannot be measured directly with a single detector because of the dead-time of the detector. It is measured in coincidence measurements between two detectors (Hanbury-Brown and Twiss setup), each of them detecting photons in a split beam. The dip of the distribution for short times is a signature of the quantum nature of the light emitted by a single molecule. It would be ruled out in a classical description of light (because the correlation of a classical function of time must always be maximal for zero time).

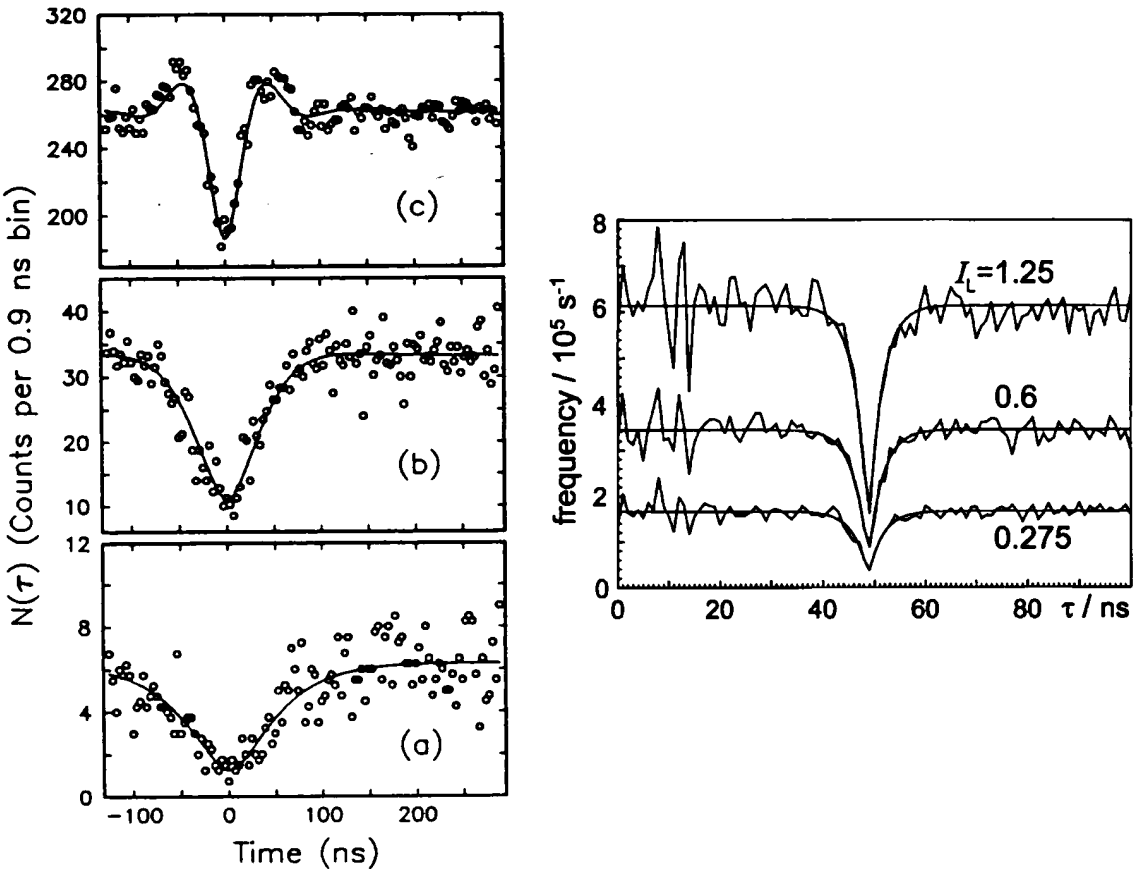


*Figure 9.7 : Example of antibunching curves at low temperature (left, from Basché et al., Phys. Rev. Lett.69 (1992) 1516) and at room temperature (right; reproduced with permission from Fleury et al. Phys. Rev. Lett. 84 (2000) 1148; Copyright 2000 American Physical Society). The main difference are the Rabi oscillations, which are observable at low temperature and high intensity only in plot c).*

The nutation transient at low temperature shows oscillations, because the laser is resonant with the transition of the two-level system. Therefore, the laser not only induces absorption, but also stimulated emission (a schematic way to visualize Rabi oscillations is to consider the interplay between these two effects). In the room-temperature experiments, on the contrary, the molecule is excited via a vibronic band, so that the laser is not resonant with the emission. Therefore, no Rabi oscillations can appear. Moreover, the damping time of these oscillations at room temperature would be on the order of some tens of femtoseconds, much too short to detect in antibunching plots.

## 9.5. Examples of quantum-optical experiments

i) Light-shift:

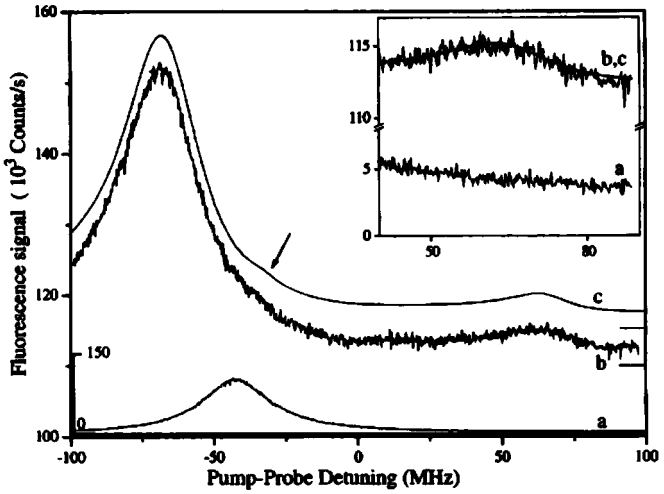


*Figure 9.8: Fluorescence excitation line of a single dibenzanthanthrene molecule without (bottom) and with (top) a strong pump intensity at frequency 0 MHz. The thin line is a calculation, and the insert shows a detail of an additional structure (from Lounis et al. Phys. Rev. Lett. 78 (1997) 3673).*

The transition frequency of an atomic or molecular system can be shifted by an electric field (Stark effect). The shift due to a light wave (light-shift) is very weak, but it can be enhanced by resonance. For the alternating electric field of a laser wave, the shift is quadratic, i.e. proportional to the intensity. It was measured by recording a single-molecule line with a weak probe beam, while a strong pump beam was used to illuminate the molecule. The results were in full agreement with optical Bloch equations [Ph. Tamarat et al., Phys. Rev. Lett. 75 (1995) 1514].

ii) Multiphoton resonances

If the intensities of pump and probe beam are comparable (e.g. equal), the Bloch vector obeys a complex dynamics in the beating field of two lasers at different frequencies. Complex structures appear in a fluorescence excitation spectrum, which can be assigned to multiphoton resonances, in which several pump and probe photons are absorbed and emitted [B. Lounis et al., Phys. Rev. Lett. 78 (1997) 3673]. Similar structures can be seen when optical and microwaves are used to illuminate the molecule, see Figure 64 [Ch. Brunel et al., Phys. Rev. Lett. 81 (1998), 2679].

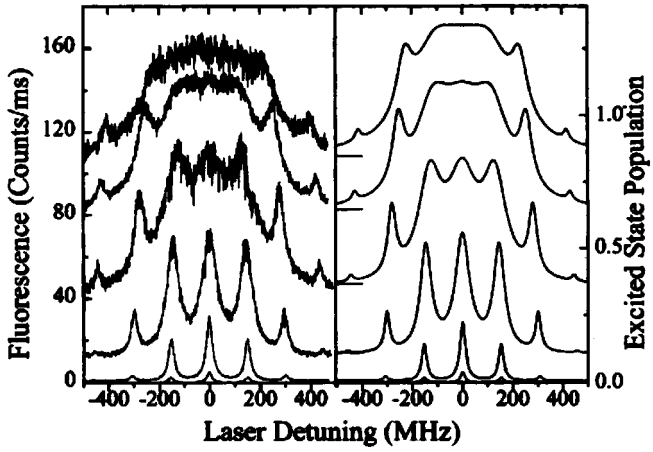


*Figure 9.9: Complex excitation lineshapes obtained when a single molecule is subject to a strong radio-frequency field. The different components are broadened and shifted by different amounts. Experiments (left) and calculations based on optical Bloch equations (right). From Brunel et al., Phys. Rev. Lett. 81 (1998) 2679.*

iii) Single-photon sources

For quantum cryptography, quantum computing, or for measurements with squeezed light, a high-rate source of single photons would be very attractive. An ideal single-photon source should deliver one and only one photon per shot. This ensures, for example, that this quantum state cannot be copied. Single molecules can work as single-photon sources. In the first work in this direction, a single molecule was swept adiabatically through resonance with a laser, which led to its excitation with a probability close to 80 %. In 70% of the sweeps, the molecule emitted one and only one photon, which is a much higher yield than with an attenuated coherent source (see Figure 9.10, [Ch. Brunel et al., Phys. Rev. Lett. 83 (1999) 2722]). Similar experiments have been performed at room temperature with a pulsed laser [B. Lounis and W. E. Moerner, Nature 407 (2000) 491].

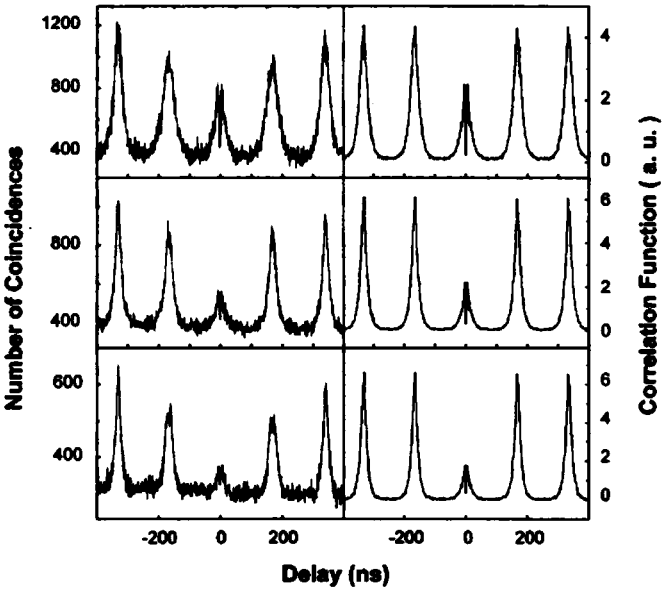


*Figure 9.10 : Autocorrelation function of the intensity delivered by a single molecule performing periodic adiabatic sweeps through the frequency of the exciting laser. The middle spectrum shows that, in 70 % of the cases, one and only one photon is emitted. Left : experimental results ; Right calculated histograms based on a quantum Monte-Carlo simulation of Bloch equations; from Brunel et al., Phys. Rev. Lett. 83 (1999) 2722 .*

Since these first demonstrations with molecules, several other individual nano-objects have been proposed as single-photon sources : color centers in diamond, conjugated polymers, semiconductor nanocrystals, and self-assembled quantum dots in heterostructures. All of these sources could be useful in applications where no coherence between photons is required. Quantum computing and teleportation experiments usually require coherent single photons. In that case, emitters have to be extremely well shielded from perturbation by their environments, which restricts the possibilities to single atoms in the gas phase and single self-assembled quantum dots. Recently, self-assembled quantum dots have been used to deliver single photons, or pairs of entangled photons, with a high rate.

*Exercise 9.1: The Bloch equations are differential equations representing the time dependence of the Bloch vector's components* $(X, Y, Z)$ *:*

$$
\begin{aligned}
\dot{X} &= -\gamma X - \delta Y \\
\dot{Y} &= \delta X - \gamma Y - \Omega Z \\
\dot{Z} &= \Omega Y - \Gamma Z + \Gamma
\end{aligned}
$$

*where the rates* $\Gamma = 1/T_1$ *and* $\gamma = 1/T_2$ *are the inverses of the longitudinal and transverse relaxation times, respectively.*
*Find the steady-state solution of this system of equations and show how it can lead to optical saturation as described above.*

*Exercise 9.2: Use second-order perturbation theory to calculate the light shift of the optical transition between ground and excited states of a two-level system, assuming the applied wave to be far detuned from the optical transition.*

*Exercise 9.3: Compare the signal-to-noise ratios in two absorption experiments, one with a classical wave and one with a stream of photons from an ideal single-photon source delivering single photons at regular intervals with the same average intensity.*