

10. Triplet state

10.1. Optical saturation with a triplet

We have discussed the optical saturation of a two-level system: the fluorescence intensity is limited by the lifetime of the excited state. Other states, especially if they are long-lived, may also limit fluorescence. This is the case of the triplet state, whose lifetime can range from microseconds to seconds for aromatic compounds. In general, no resonant level can be reached from the triplet state by absorption of a laser photon (triplet-triplet absorption can take place, but it is not resonant, and triplet-triplet fluorescence often has very low quantum yield). Therefore, a molecule in the triplet state is virtually dark, i.e., non-fluorescent. This limitation of fluorescence by the triplet will be more severe for high triplet yield η_T (branching ratio from the excited singlet) and for long triplet lifetime τ_T . For a triplet yield much smaller than unity, the maximal number of photons per second a molecule can emit is about $(\eta_T \tau_T)^{-1}$, i.e. 1 million per second for a yield of 10^{-3} and a lifetime of 1 ms. These conditions on the triplet parameters severely limit the number of compounds which can be useful in single-molecule spectroscopy and microscopy.

The triplet « state » is in fact a manifold of three sublevels. Even in zero magnetic field, the degeneracy of the three sublevels is lifted, mainly by magnetic dipole-dipole interactions between the unpaired electrons. For a molecule with D_{2h} symmetry (which is the case of several aromatic hydrocarbons, for example pentacene or terrylene), the spin eigenstates can be labelled according to the molecular axes, the state $|X\rangle$ having its spin polarized in the (Y, Z) plane, perpendicular to axis X . Z is usually chosen as the axis normal to the molecular plane. The energy splitting between state Z and the middle of X and Y , called D , is on the order of a few GHz, while the half of the X - Y splitting, called E , is significantly lower, usually less than a GHz (see scheme in Fig. 10.1). Because the matrix elements of the spin-orbit coupling depend on spin orientation with respect to the orbital, the three sublevels have in general different population rates from the excited singlet, and different relaxation rates towards the ground singlet. Usually, the Z -state is less coupled than the other two.

$$D = \epsilon_z - \frac{1}{2} (\epsilon_x + \epsilon_y)$$

$$E = \frac{1}{2} (\epsilon_x - \epsilon_y)$$

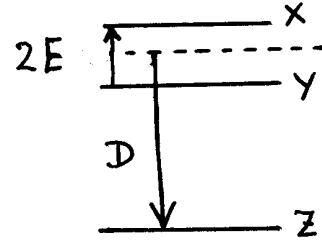


Figure 10.1 : Level scheme of the triplet sublevels split by the anisotropic dipolar interaction. The D and E parameters are the energy differences defined in the diagram.

The optical saturation in the case of a triplet has the same form as that of the two-level system, but the saturation intensity, and the maximal number of counts at saturation are both *reduced* relative to their values for the two-level system by the factor :

$$\xi = 1 + \frac{1}{2} \sum_i \frac{a_i}{b_i} = 1 + \frac{1}{2\tau_f} \sum_i \eta_i \tau_i, \quad [10.1]$$

where the sum runs over the triplet sublevels, and a_i (b_i) are the population (depopulation) rates of each sublevel from (to) the excited (ground) singlet state, equivalently expressed with the respective triplet yields and triplet lifetimes. τ_f is the fluorescence lifetime.

10.2. Photon bunching

The shape of saturation curves is the same for two and three-level saturation. It is therefore impossible from a saturation analysis alone to conclude about the role of the triplet state. To find this, we need further information, which must be of a dynamical, or time-dependent nature. In other words, the saturation only provides us with a ratio of population and depopulation rates (see the expression of ξ), but we have to find at least one of the rates to determine both of them.

A convenient way to obtain this time-dependent information is to record a correlation function of the fluorescence intensity. As we have seen earlier in our discussion of photon bunching, excursions of a single molecule into its triplet dark state lead to strong fluctuations of its fluorescence intensity. For a single triplet sublevel, the analysis is identical to the one we presented for room temperature, and leads to a single exponential decay in the normalized correlation function:

$$g^{(2)}(\tau) = 1 + \frac{k_{13}}{k_{31}} e^{-(k_{13} + k_{31})\tau} \quad [10.2]$$

where k_{31} is the decay rate of the triplet state to the ground singlet, and k_{13} is the effective population rate of the triplet state, which can be expressed as a function of the Rabi frequency, the relaxation times and the intersystem crossing rate k_{23} :

$$k_{13} = \frac{k_{23}}{2} \frac{\Omega^2 T_1 T_2}{1 + \Omega^2 T_1 T_2}. \quad [10.3]$$

In case two or three triplet sublevels must be considered, the solution of Bloch equations leads to two or three exponential components in the correlation function. Because relaxation to the ground state couples the different sublevels, the rates appearing in the exponentials take on more complicated forms than in the simple mono-exponential case above. In many cases, the parameters of the X and Y sublevels are too close to distinguish them in experimental data. Then an effective triplet state with two sublevels suffices to fit the correlation function with a bi-exponential decay. Figure 10.2 shows the intensity dependence of the contrasts and decay rates of the two exponential components in the correlation function of a single DBATT molecule in a hexadecane matrix.

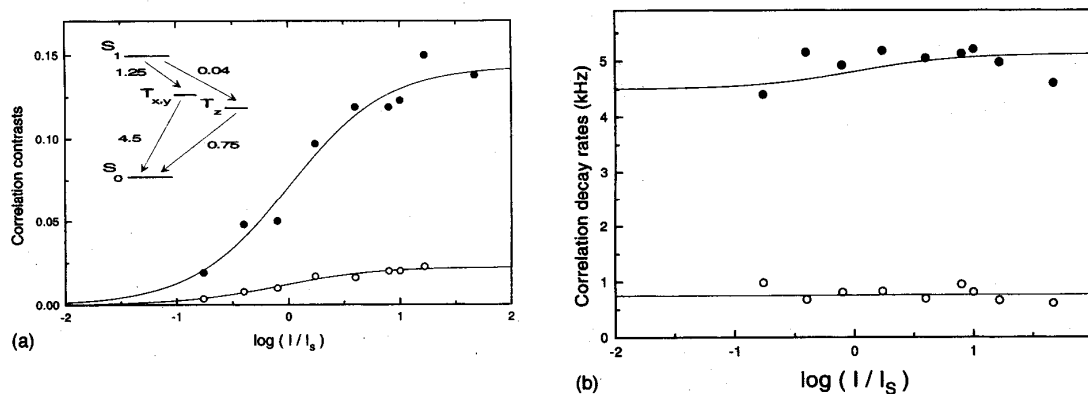


Figure 10.2 : Contrast (a) and rates (b) of the two exponential components in the correlation function of a single DBATT molecule. The population and depopulation rates of the triplet deduced from these plots are shown in the insert [A.-M. Boiron et al. *J. Chem. Phys.* 105 (1996) 3969].

An alternative way of obtaining dynamic information about the triplet state is to directly observe the on- and off-times in the fluorescence signal. This is particularly efficient in the case of weak intersystem crossing rates, if the dark intervals have sufficient duration. These direct observations were first made on a single terrylene molecule in a p-terphenyl crystal (see Fig. 10.3). Building histograms of on- and off-

times, one directly obtains the above two rates k_{13} and k_{31} , and hence the triplet lifetime and the intersystem crossing rate.

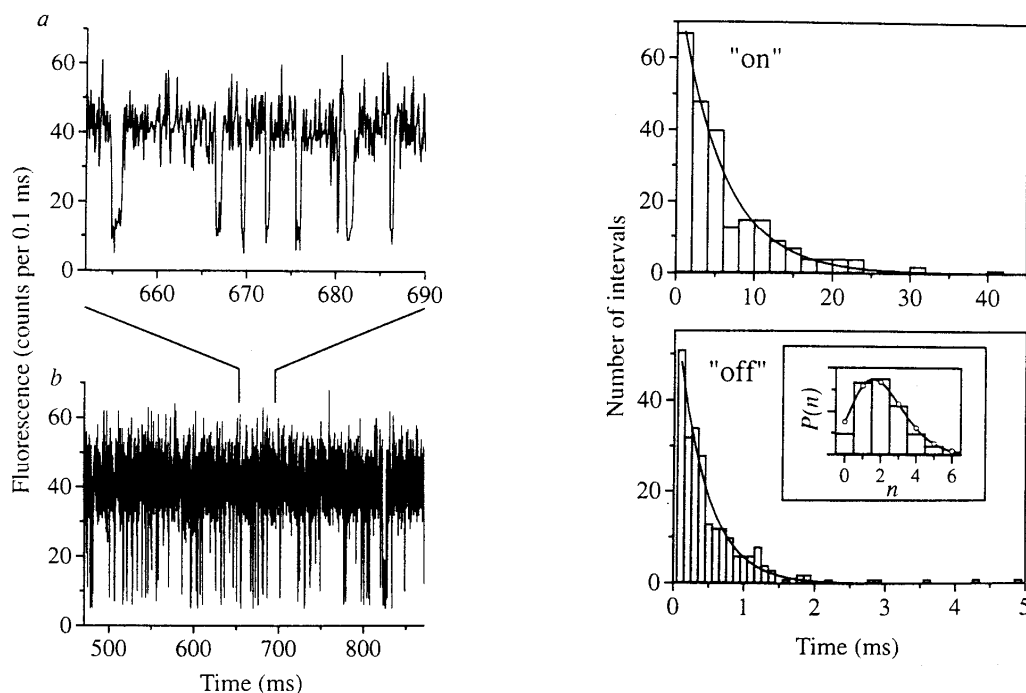


Figure 10.3 : On- and off-times in the fluorescence signal of a single terrylene molecule excited above saturation of the three-level system. The histograms of on- and off-times provide the population and decay rates of the triplet [Reproduced with authors' permission from Th. Basché, S. Kummer, Ch. Bräuchle, *Nature* 373 (1995) 132].

10.3. Optically detected magnetic resonance

Magnetic resonance is achieved when the spin state is changed under microwave irradiation. In usual experiments, the spin levels are split in a static magnetic field, but the triplet sublevels of molecules are split by dipole-dipole magnetic interactions (zero-field splitting). Because of the different influence of each spin sublevel on optical saturation, the average fluorescence intensity will be changed if the occupation of the sublevels is modified. This opens the opportunity to observe magnetic resonance via variations of the fluorescence intensity.

Figure 10.4 presents the variations of the fluorescence intensity of a single pentacene molecule in a p-terphenyl crystal when a microwave is tuned in a range between 1.3 and 1.5 GHz. The two dips are due to microwave Y-Z and X-Z transitions. The fluorescence change upon the X-Y transition was too weak to be detected. The characteristic asymmetric shape of the dips is mainly due to hyperfine interactions

with the spins on the 14 protons in the pentacene molecule. Hyperfine interactions contribute in second-order perturbation, and lead to further splitting of the X and Y sublevels. The sharp edges corresponds to zero total spin of the protons, which is the most likely configuration.

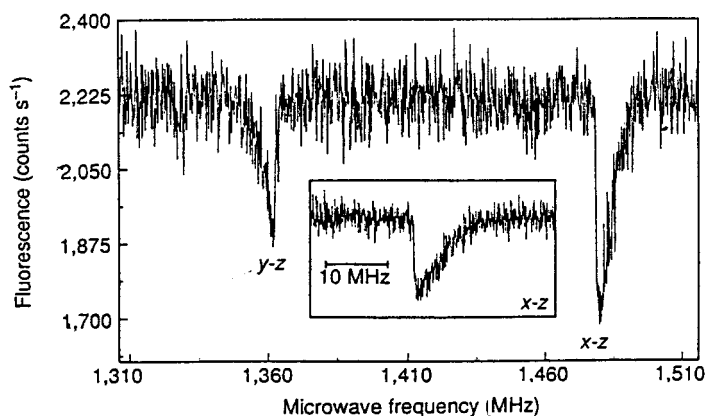


Figure 10.4 : Optically detected magnetic resonance of a single electronic spin. The fluorescence intensity of a single pentacene molecule excited at saturation shows dips when an applied microwave frequency coincides with transitions between triplet sublevels [J. Wrachtrup et al., *Nature* 363 (1993) 244 ; see also J. Köhler et al., *ibid.* 242] .

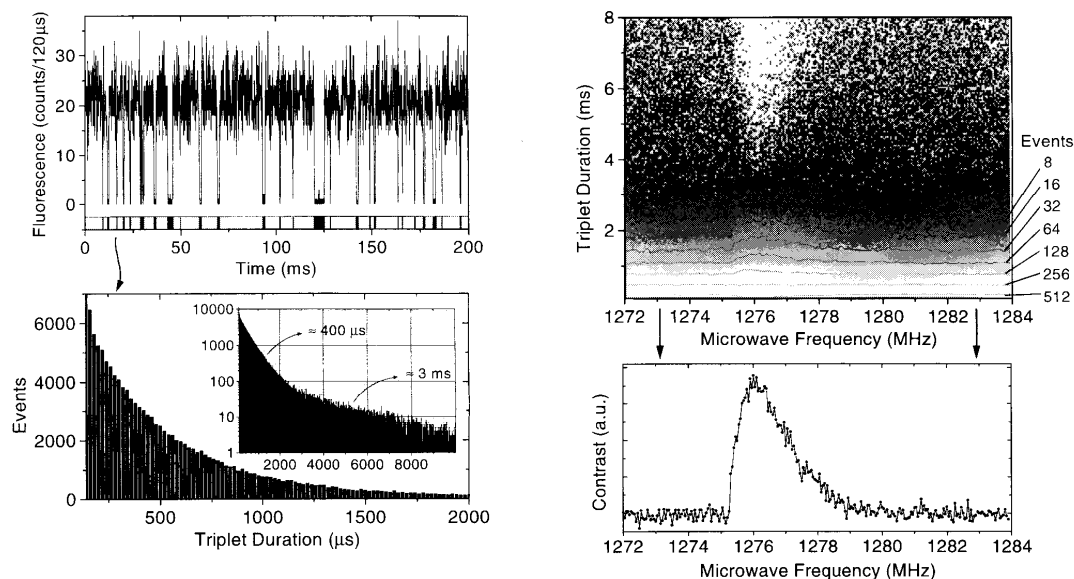


Figure 10.5 : Detection of magnetic resonance via the distribution of off-times (triplet duration). The method is much more sensitive than the average intensity, because it focuses on a few events, disregarding the noisy bright periods [Reprinted with permission from A. C. J. Brouwer et al. *Phys. Rev. Lett.* 80 (1998) 3944. Copyright 1998 American Physical Society].

Under microwave illumination, the fluorescence correlation function is deeply changed. The long-lived component due to the Z sublevel is dramatically shortened,

because the spins are brought back to the X or Y sublevels, where relaxation towards the ground state is fast. This analysis gives access to magnetic resonance, even in the cases where the fluorescence variation would be too small to detect. Brouwer et al. have observed the ODMR of a single terrylene molecule in p-terphenyl in this way, as well as the spin nutation (see Fig. 10.5).

10.4. Single nuclear spins

Figure 10.4 shows how the ODMR signal of a molecule is influenced by the spin state of the protons. Because the recording of the ODMR line lasts several minutes, the nuclear spins are sampling a large number of configurations, which fluctuate with a characteristic time of milliseconds. This dynamics of the nuclear spins leads to a spectral diffusion of the electron spin line. If the protons in the guest molecule and in the matrix are replaced by deuterons, which have a six times smaller magnetic moment, the second-order hyperfine interaction -and the ODMR linewidth- is reduced by a factor 36, giving rise to much narrower lines. A pentacene molecule contains 22 carbon atoms, and therefore has a probability of about 10% to contain a ^{13}C atom in natural abundance. The spin of the ^{13}C atom is also flipping as time goes, which leads to a spectral diffusion of the ODMR line between two positions, corresponding to two orientations of the nuclear spin with respect to the electron spin. This splitting has been observed on the ODMR spectra of single molecules. In this way a single nuclear spin is detected.

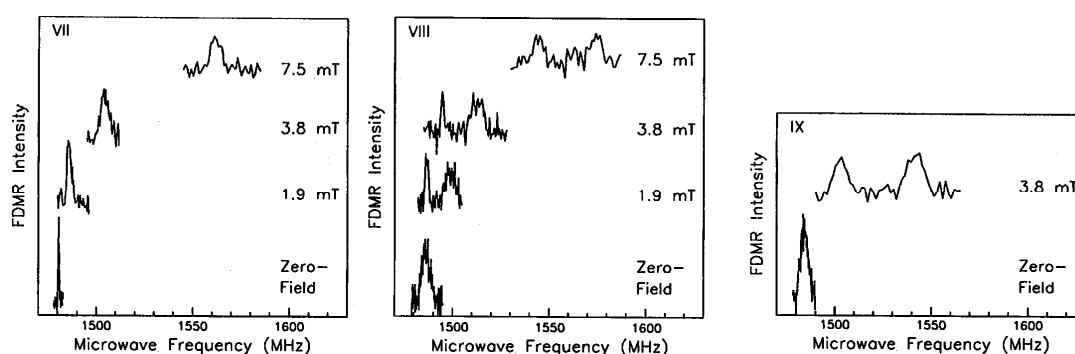


Figure 10.6 : ODMR spectra of fully deuterated single pentacene molecules containing only $\text{C}12$ atoms (left), or one $\text{C}13$ atom in two different positions (center, right). The splitting of the line under field is due to the two states of the nuclear spin [Reproduced with permission from J. Köhler et al., *Science* 268, 1995,1457. Copyright 1995 AAAS].

It was proved possible to go one step further, and to manipulate the nuclear spin with a resonant RF wave. In the same way the electronic transition is used to probe the electron-spin transition by ODMR, the electron spin transition can be monitored as the RF frequency is tuned in the range of nuclear spin transitions in an applied magnetic field, in a so-called ENDOR (electron-nuclear double resonance) experiment. It turns out that the ENDOR signal is too weak to detect with cw illumination by microwave and RF wave. However, if a $\pi/2$ microwave pulse and RF pulses are applied, the ENDOR signal can be considerably enhanced, and be detected for a single molecule. Such spin manipulations are very promising for quantum computing and quantum network applications, since quantum states can be stored on much longer times by electronic spins (lifetimes ms) and nuclear spins (lifetimes of s) than by electronic states (lifetimes of ns).

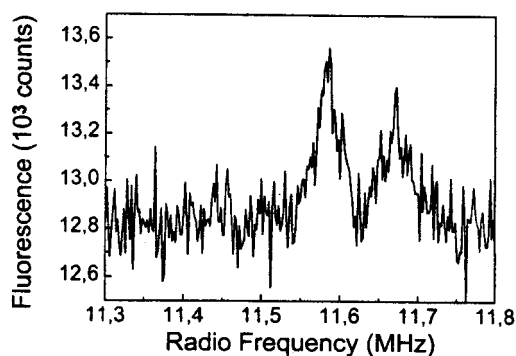


Figure 10.7 : ENDOR spectrum corresponding to the nuclear resonance of a single proton in a pentacene molecule containing two protons and twelve deuterons [Reprinted from J. Wrachtrup et al., *Chem. Phys. Lett.* 267, 1997, 179. Copyright 1997 with permission from Elsevier].

10.5. NV-center in diamond

The level diagram of the nitrogen-vacancy (NV) center in diamond has ground and excited triplet states and a metastable triplet state. This also leads to ODMR signals that are visible at room temperature and have been used for nuclear spin manipulations (see work of R. Hanson at TU Delft).