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Optically Detected Spin Coherence of Single Molecules

J. Wrachtrup,[1] C. von Borczyskowski,[2] J. Bernard,[3] M. Orrit,[3] and R. Brown[3]

[1]*Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, 14195 Berlin, Germany*
[2]*Technische Universität Chemnitz, Fachbereich Physik, Reichenhainer Strasse 70, 09126 Chemnitz, Germany*
[3]*Centre de Physique Moléculaire Optique et Hertzienne, Centre National de la Recherche Scientifique,*
Université de Bordeaux I, 351 Cours de la libération, 33405 Talence, France

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Optically detected electron paramagnetic resonance of single molecules of pentacene in a *p*-terphenyl crystal at 1.8 K is presented. Transient nutation of a single electronic spin is demonstrated, showing a coherence damping within several microseconds. The fluorescence photons of a single molecule can be used as an internal time base to trigger the application of microwave pulses. Because of this it is possible to enhance or switch off the optically detected magnetic resonance effect, depending on the delay between the triggering photon and the microwave pulse.

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Magnetic resonance is a spectroscopic technique widely used in physics, chemistry, biology, and medicine because its higher spectral resolution, compared, for example, to optical spectroscopy, can provide detailed information on the structure, electronic wave function, and the spin dynamics of the compound under study. However, this advantage is offset by a lower sensitivity: One has to use ensembles of approximately 10^9 or 10^{12} spins for electron paramagnetic (EPR) resonance, or 10^{16} to 10^{19} for nuclear magnetic resonance (NMR) of ensembles in Boltzmann equilibrium [1]. By using optical detection of magnetic resonance (ODMR) one usually gains several orders of magnitude in sensitivity. The threshold sensitivity may then be as low as 10^4–10^5 spins in a nonequilibrium sample [2]. Sensitivity to even one single electronic spin was recently demonstrated for the chromophore pentacene (Pc) substitutionally incorporated into a single crystal of paraterphenyl (PT), by combining ODMR methods with single molecule spectroscopy [3,4].

Figure 1 depicts the basic energy level scheme, relevant for single molecule spectroscopy. In this method, a continuously excited molecule performs absorption-emission cycles between the ground ($^1S_0$) and first excited ($^1S_1$) singlet state. This is achieved by tuning a narrow band laser to the absorption line of a single molecule in the inhomogeneously broadened absorption profile of very dilute chromophores in organic solids, in our case $\sim 10^{-9}$ mol/mol Pc in PT, at low temperatures. The first successful single molecule detection via fluorescence excitation spectroscopy has been reported for the same system, Pc in PT [5,6].

In order to understand the basic principle of single spin detection by ODMR we have to consider (Fig. 1) the role of the lowest excited triplet state. During the excitation-emission cycle the molecule occasionally crosses from the diamagnetic $^1S_1$ state to the longer lived, nonemissive triplet state $^3T_1$, with total spin $S=1$. Thus, bursts of fluorescence are interrupted by dark periods when the molecule is in the triplet state. The time spent in this state depends on which of the $2S+1=3$ spin sublevels is populated, since they generally have different lifetimes and population rates due to the symmetry-selection rules of the involved spin forbidden transitions. A change in the average fluorescence intensity (ODMR effect) can be obtained by applying a resonant microwave (MW) field to pump the molecule between spin sublevels with different lifetimes, which consequently changes the average duration of the dark intervals.

While the experiments with continuous MW irradiation will have interesting analytical applications in the future, we draw attention here to another advantage of single molecule ODMR, that is, the possibility to observe coherent transients on a single quantum system. Here we will call coherence any behavior whose observation requires the preparation of a quantum superposition of states. In conventional experiments on ensembles, the composing entities must first be brought into phase with each other by an external pulse. For single quantum systems, coherence can be observed even under continuous excitation, as was demonstrated some years ago for single atoms [7] and more recently for a single molecule in a solid [8]. The conventional interpretation of coherence,

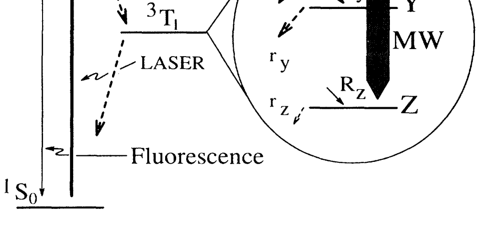

FIG. 1. Energy level scheme showing the singlet ground state $^1S_0$, the first excited state $^1S_1$, and the lowest excited triplet state $^3T_1$. The energy separation of $^1S_1$ and $^1S_0$ is ~ 16883 cm^{-1}; that of $^3T_1$ and $^1S_0$ is estimated to be ~ 10000 cm^{-1} [17]. Populating and depopulating rates of the triplet sublevels are denoted by $R_{X,Y,Z}$ with $R_X \sim 66$ kHz, $R_Y \sim 29$ kHz, $R_Z \sim 0.28$ kHz, and $r_{X,Y,Z}$ with lifetimes $r_{X,Y}^{-1} \sim 47$ μs and $r_Z^{-1} \sim 830$ μs, respectively [10].

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deriving from the density matrix formalism, applies to ensembles only. A single quantum system can perform quantum jumps which the density matrix formalism fails to reproduce. However, coherence effects may be observed even for a single system after averaging over a time period much longer than all relevant time constants (in a similar way the observation of fringe patterns with Young's slits demands many particles). By means of this ergodic hypothesis we therefore may treat time averages of a single quantum system with the density matrix of an ensemble.

In this communication we will concentrate on what we believe are the basic properties of spin coherence and its dephasing processes of a single molecule.

The optical setup and the sample preparation have been described elsewhere [5]. The light of a single mode ring dye laser is transmitted to the 10 μm thick sublimation grown PT crystal by means of a single mode optical fiber. The fluorescence from the Pc chromophore is collected efficiently by a parabolic mirror, passed through a red pass and notch filter, and detected via single photon counting. All measurements reported here were done at a temperature of $T \sim 1.8$ K.

MW are applied by means of a coax cable. The inner conductor of this cable was grounded to the shield by a loop with a diameter of approximately 3 mm. The sample mounted on the fiber was placed in the center of this loop, in the focus of the mirror. For the pulsed ODMR experiments, the MW are switched by a pair of pin diodes, driven by a pulse generator with 10 ns time resolution. In some cases the start of a pulse sequence was triggered by pulses from the amplifier discriminator of the photon counter, that is, by photons emitted by the single molecule itself.

The ODMR experiments were carried out by tuning the laser frequency to the absorption line of single Pc molecules, mostly in the red wing of the so-called O_1 line [5] between 592.42 and 592.59 nm. The fluorescence was monitored during repetitive microwave frequency scans of 10 s duration. A typical acquisition time for a spectrum like the one shown in Fig. 2 was about 20 min. All experiments were performed without the application of an external magnetic field.

Figure 2 shows an ODMR spectrum, i.e., the fluorescence intensity as a function of the MW frequency in the region of two of the three expected resonant spin transitions, classified according to the molecular symmetry axes X, Y, and Z.

The line shapes of both transitions are highly asymmetric. For the X-Z transition the steep increase of the fluorescence intensity takes place in an interval of 300 kHz, which is close to the homogeneous linewidth [9]. The line shapes are similar to those observed for an ensemble of Pc in PT, where it is determined mainly by the second order hyperfine interaction (HFI) of the electron spin with proton spins of the Pc molecules [3,4]. Although a single molecule is at a given time in only one of its combined electron-nuclear spin states, with an ODMR transition related to a homogeneous linewidth of about 200 kHz, the spectra clearly indicate that several, or all, electron-nuclear spin states show up during the detection time, which has been at least 2 min. This can be attributed to a spectral diffusion process of those nuclear spins responsible for the HFI which are allowed to change their spin states while the molecule is in the singlet manifold [3,4].

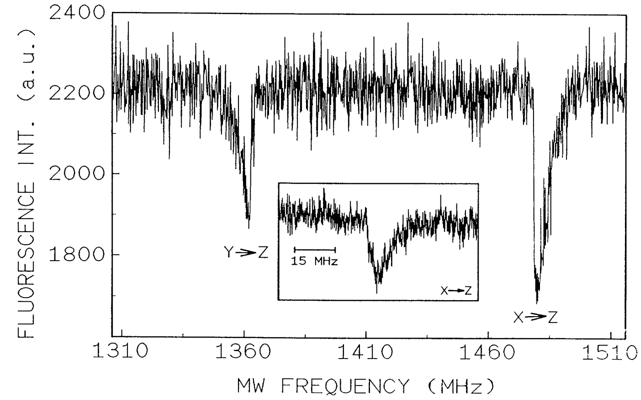

FIG. 2. ODMR spectrum in the region of the Y-Z and X-Z transition for an O_1 site molecule. The inset shows the X-Z transition on an enlarged scale for a region in the absorption spectrum where several molecules contribute to the ODMR spectrum. The sharp structure present in the single molecule case is smoothed out. In addition a shoulder appears on the low frequency side of the line, most probably due to molecules with slightly different zero field splitting parameters, more characteristic for the O_2 site [3].

We now turn to the observation of spin coherence: Figure 3 shows a transient spin experiment, in which we monitored the fluorescence of a single molecule while increasing the width of the resonant microwave pulse from 0.02 to 1.7 μs. During the pulse, the spin is coherently driven between the $|X\rangle$ and $|Z\rangle$ levels by the MW field with a Rabi period $\omega_1 = \gamma B$ of $\sim 2\pi \times 5$ MHz at an incident MW power of 20 W (γ is the gyromagnetic ratio and B the magnetic field component of the MW). The repetition rate of the MW pulses is 200 Hz. The fluorescence intensity is sampled for 1 ms after the pulse. The variation of the fluorescence intensity reflects the lifetime of the sublevel in which the electronic spin is left at the end of the MW pulse, starting in the $|X\rangle$ and reaching the $|Z\rangle$ level for a perfect π pulse with a length of ~ 100 ns. For all investigated molecules we find that the transient spin nutations start with the same phase, i.e., at the maximum fluorescence intensity or in other words in the $|X\rangle$ level. Furthermore, for different molecules the measured nutation patterns are damped within a time varying between 2 and 5 μs.

Apparently the nutation pattern presented in Fig. 3 mimics the density matrix evolution of an ensemble. This is because of the long accumulation time needed to obtain

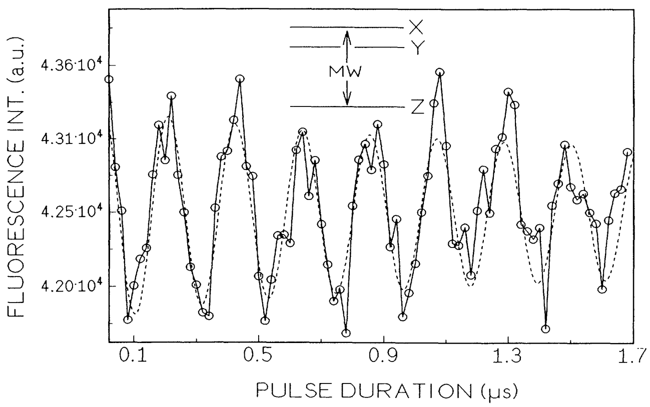

FIG. 3. Transient nutation of the X-Z transition. Average incident MW power is about 20 W. Circles represent measured values and lines are merely guidelines. The resolution is 0.02 μs. The dotted line represents a simulation of the transient nutation (see text).

a sufficient signal to noise ratio resulting in a time average which is equivalent to an ensemble average, according to the ergodic hypothesis.

It is well known [11] that the transient nutation experiment provides information about relaxation of the magnetization, that is, the longitudinal relaxation time T_1, or the transversal relaxation time T_2 via the damping of the nutations. For triplet states like the one investigated here, T_1 is known to be long compared to T_2 at temperatures of ~ 1.8 K. However, for molecular ensembles, experimental imperfections, namely, the inhomogeneity of the static magnetic field and the MW B field, often determine the damping time of the nutations [11]. In the case of a single molecule no such field inhomogeneities have to be considered. The damping of the oscillations therefore depends only on intrinsic properties of the molecule and its interaction with the embedding solid. One possible reason for the damping of the nutations is the spread of frequency differences between the carrier frequency of the pulse and the actual resonance transition frequency of the molecule within the quasi-inhomogeneous line. Assuming ergodicity and according to well known concepts when dealing with ensembles [12], this variation of frequency differences results in a damping of the transient nutation. For the situation under study, that is, $\omega_1/\Delta\omega_{1/2} \cong 1$ (with $\Delta\omega_{1/2}$ for the ODMR linewidth), we derive a damping time of ~ 5 μs, as is shown by the simulation included in Fig. 3.

Another reason for the damping might be the loss of phase relation due to transverse (T_2) relaxation of the magnetization, which in our case has to be defined as the loss of phase memory of the triplet spin under study with respect to the fixed phase of the driving MW field. In comparison with known results from ensemble experiments [9], these T_2 processes are expected to give rise to a damping of the transient nutation on a time scale similar to the one mentioned before. Thus both effects might contribute to the observed damping of the transient nutations.

A way to eliminate the effect of the quasi-inhomogeneous ODMR line on the dephasing of the single spin is to use an appropriate MW pulse sequence. Such a pulse sequence is the Hahn-echo two-pulse experiment. Preliminary results of this type of experiment on the single triplet spin systems yield a dephasing time of ~ 3 μs with a dispersion of this value for different molecules of approximately ± 1 μs.

We have presented so far methods known from conventional coherent magnetic resonance experiments on an ensemble of molecules. We now report an experiment which can be performed only on a single molecule, because it makes use of the excited state of the molecule as an internal clock to trigger the application of MW pulses. This possibility is related to the fact that the fluorescence of a single molecule is emitted in bunches, whose time width (which can be deduced from the decay time of the fluorescence correlation function [13]) depends on the optical pumping rate, the average decay rate from ${}^1S_0$ to ${}^1S_1$ and the ISC rate, k_{ISC} from ${}^1S_1$ to ${}^3T_1$. In the limit of optical saturation, the width amounts to about $2/k_{\mathrm{ISC}} \sim 10$ μs in this system [13]. Emission of light indicates that the molecule is in the singlet manifold, so application of a MW pulse at this time will have no influence on the fluorescence intensity. On the other hand, triggering the MW pulse on the emission of a photon with a delay between the trigger and the pulse larger than the average width of the bunches but shorter than the triplet lifetime will synchronize, on average, the pulses with the crossover of the molecule from ${}^1S_1$ to ${}^3T_1$. This offers the possibility to switch off or enhance the ODMR effect in contrast to pulsed MW excitation of an ensemble, where there is no possibility to establish a phase relation between the molecules and the MW in an optically continuously excited sample.

Figure 4 shows the ODMR effect for different delay times of the photon triggered MW pulses. The inset of the figure shows the development of the fluorescence after the pulse has been applied, representing one data point in the main figure. The ODMR effect has been taken as the decrease in fluorescence below the steady state value indicated by the dotted line in the inset. The principle of the measurement is analogous to the classical inversion recovery known from ensemble experiments [14]. After the inverting MW pulse the fluorescence approaches the steady state value with a time constant of approximately 830 μs corresponding to the lifetime of the $|Z\rangle$ level. In contrast to the classical fluorescence recovery experiment, however, there is an initial steep decrease in fluorescence (first 20–40 μs), which is also absent in a nontriggered inversion recovery experiment on a single triplet spin. This is the signature of photon bunching. Its importance decreases at longer delays as the pulse moves out (on average) of the bunch containing the triggering photon.

As is expected from the discussion, the ODMR effect is

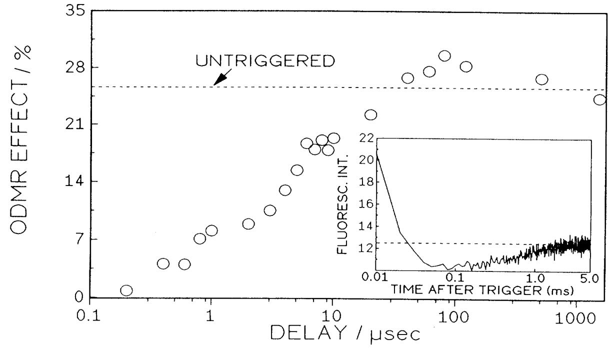

FIG. 4. ODMR effect as a function of the delay time between the triggering photon and the MW π pulse with a length of 100 ns. The inset shows the time resolved fluorescence intensity after the trigger has been initiated. The time resolution is 10 μs and the delay time 9 μs. The repetition rate of the experiment is 200 Hz. The dotted line in the main figure indicates the magnitude of the ODMR effect for π-pulse excitation not triggered to the emission of photons.

indeed weak for delay times shorter than the average duration of the bunches, because of the high probability of the molecule still being in the singlet manifold. It is enhanced for delays of the order of the intersystem crossing time, because there is a high probability of having crossed over to the triplet manifold when the pulse is applied. As can be taken from the figure there is a slight enhancement of the ODMR effect of about 10% comparing the maximum triggered ODMR effect with the untriggered one. For still longer delay times any phase relation between the application of the MW pulse and the excitation-emission cycle is lost; hence the ODMR effect approaches the nontriggered value, as is observed.

In conclusion, we have shown that for a single molecule it is possible to synchronize the application of MW pulses to photons emitted from the molecule. This experiment can be performed only when the photons come from one single emitter and can be taken as a further hint for the presence of a single electron spin.

The presented experiments demonstrate that via optically detected magnetic resonance the wide range of pulsed EPR methods is applicable to studies on single molecules. In contrast to optical molecule spectroscopy, ODMR spectra are characterized by a quasi-inhomogeneous line due to HFI, which has impact on some of the spin coherent experiments. Spin-echo experiments, however, can overcome this limitation. Access to spin dephasing times (e.g, T_2) of a single molecule will probe the dynamics of the nanoscopic magnetic environment, providing a strong test of theories on spin dynamics in the triplet state. In addition, such measurements could characterize the embedding solid in far more detail compared to ensemble experiments, which has already been shown by optical single molecule experiments [6,15]. Single spin ODMR will add the aspect of magnetic interaction to this newly developed field of spectroscopy.

Because of the optical detection procedure present experiments are limited to excited triplet states. However, extensions to ground state nuclear polarization followed by NMR experiments may be envisaged. A more severe drawback is the limitation to molecules with a sufficiently large absorption cross section and fluorescence quantum yield together with a high photostability of the guest/host system [5], which limits single molecule spectroscopy to a presently small class of molecules and matrices. In addition, a sufficient ODMR effect imposes restrictions on the relative population— and depopulation rates of the triplet state of the chromophore [16]. For those systems meeting the above requirements extension to various methods of magnetic resonance is expected, including studies in static external magnetic field and electron-nuclear double-resonance techniques. Orientation dependent investigations on single molecules in disordered matrices will become feasible. Studies on molecules embedded in ultrathin films and on surfaces may be expected in the near future. The main application of this technique and its magnetic resonance variants will be the field of very sensitive probes for their nanoscopic environment. Besides these applicational aspects single molecule magnetic resonance is an intriguing conceptional experiment in that it probes predictions from ensemble experiments on a true molecular base.

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